# INTRODUCTION TO
# STATISTICAL
# THERMODYNAMICS

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# INTRODUCTION TO STATISTICAL THERMODYNAMICS

By

MALCOLM DOLE

Professor of Chemistry
Northwestern University

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# PREFACE

In 1940, at the time of the founding of the Northwestern Technological Institute, the curriculum of the Chemistry Department in the College of Liberal Arts was modified to meet its own expanding needs and those of the newly established Department of Chemical Engineering. Since that time the first advanced courses of physical chemistry beyond the elementary course have consisted of courses in thermodynamics, statistical thermodynamics, and kinetics, offered in the order listed. The subject matter of two of these courses has appeared in book form; the first to appear was *Chemical Thermodynamics* by Professor Klotz,[1] and the second, *Kinetics and Mechanism* by Professors Frost and Pearson.[2] The trilogy has been completed by the publication of this book on statistical thermodynamics.

Statistical thermodynamics is the subject that bridges the gap between thermodynamics and kinetics on the one hand and, even more important, between chemistry and physics on the other. Thus in chemistry we observe, measure, tabulate, and classify the *average* behavior of a vast number of molecules and mixtures of molecules, but in physics it is the properties of *individual* molecules, such as their masses, energy states, frequencies of vibration, and moments of inertia, which are studied. The reflective student of physical chemistry and thermodynamics is at times concerned with how energy states of molecules, such as the electronic, rotational, and vibrational states, are related to specific heats, heats of reaction, and other thermal properties of chemical substances. It is the study of statistical thermodynamics that will clarify these relationships.

As J. E. Mayer[3] has remarked, "It is widely agreed that no student understands physical chemistry until he has completed a logical course in thermodynamics." Similarly, no student really understands thermodynamics until statistical thermodynamics or

[1] I. M. Klotz, *Chemical Thermodynamics*, Prentice-Hall, Inc., New York, 1950.

[2] A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, John Wiley & Sons, Inc., New York, 1953.

[3] J. E. Mayer, *J. Chem. Ed.*, **22**, 11 (1945).

statistical mechanics has been studied. Statistical mechanics is the foundation on which statistical thermodynamics is built. However, this book contains a minimum of statistical mechanics for an understanding of its applications to thermodynamics. For example, the Boltzmann *H*-theorem, which has been of such great importance in classical statistical mechanics is omitted, and the Bose-Einstein and Fermi-Dirac statistics are briefly treated. Canonical ensembles, grand partition functions, the method of steepest descents, statistics of condensation are not discussed, and the fundamentals of quantum statistical mechanics are briefly introduced. The reasons for minimizing the former are, first, the subject of statistical mechanics can only be taught properly in a course devoted to this subject and after adequate courses in classical and quantum mechanics; second, in a one-quarter course for chemists, it has seemed best to concentrate on applications of chemical interest; and finally, few, if any, of the students who take a course in statistical thermodynamics, including organic chemists, have the mathematical or theoretical background necessary for an understanding and appreciation of statistical mechanics. Although most of the physical chemists later acquire a good knowledge of statistical mechanics in the year course taught in the Department of Physics, for many of the students enrolled in statistical thermodynamics this is a terminal course.

In order to stimulate the interest of the student in the subject, examples of practical applications have been introduced as quickly as possible. For example, after Chapter II, which describes briefly some mathematical aspects of probability, a discussion of the distribution of molecular weights in linear condensation-polymers based on probability considerations is given. This chapter may be omitted if desired, since it is unnecessary for an understanding of the chapters that follow. Chapter VI, on the interionic attraction theory of strong electrolytes, is in a similar category.

As is universally recognized, student problems have a great importance in the teaching of statistical thermodynamics; in fact, the examinations given in the course at Northwestern are invariably of the open book type. There are included in the book, therefore, many problems which have been collected over a number of years.

The author initiated the teaching of statistical thermodynamics at Northwestern in 1937 in a seminar for advanced students of physical chemistry. His organization of the material at that time

and ultimately the preparation of this volume were greatly aided by the loan of notes on statistical mechanics by Professor J. G. Kirkwood when he was a member of the University of Chicago faculty, and by the late Dr. Albert Sherman. To both of these men he is greatly indebted. As will be immediately seen on reading this book, the author has drawn heavily from the great work of Fowler and Guggenheim on statistical thermodynamics, from Schrödinger's little book on the same subject, and from the well known and important books by Mayer and Mayer and by Gurney on statistical mechanics.

The author is grateful to Dr. G. Herzberg, author of the *Spectra of Diatomic Molecules* for permission to make use of Figs. 51, 58, and 59 of his book; to the Editor of the *Journal of the American Chemical Society* and to Drs. F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling, and G. W. Vinal for permission to reprint the data contained in Table 1 of the Appendix; to Dr. E. Wichers for supplying the latest table of atomic weights in advance of publication; to Drs. A. O. Nier and T. L. Collins for a table of isotopic masses; to John Wiley and Sons, Inc., for permission to reprint the energy conversion factors and isotopic spin data contained in Tables 4 and 3 of the Appendix; to the Williams and Wilkins Co. for permission to reprint the table of Einstein functions, Table 5 of the Appendix; to the Editor of the *Journal of Chemical Physics* and to Drs. J. Bigeleisen and M. G. Mayer for permission to reprint the values of the *G*-function given in Table 6 of the Appendix.

Finally, the difficult job of typing done by the Señorita Lía Carranza of the Argentina Ministry of Public Health while on a sabbatical visit to this country in 1952–53 is gratefully acknowledged.

MALCOLM DOLE

*Evanston, Illinois*

# CONTENTS


1. INTRODUCTION *1*

1-1. The fundamental basis of thermodynamics..... 1
1-2. The fundamental basis of statistical mechanics..... 2
1-3. Statistical thermodynamics and its relation to statistical mechanics and thermodynamics..... 7

2. INTRODUCTION TO MATHEMATICAL PROBABILITY *10*

2-1. Definitions: mathematical probability..... 10
2-2. The theorems of total and compound probability..... 11
2-3. Permutations, combinations, complexions, examples .. 13
2-4. The problem of repeated trials, binomial theorem, *a priori* probability, statistical weight..... 17
2-5. Properties of factorials..... 21
Problems..... 21

3. DISTRIBUTION OF MOLECULAR WEIGHTS IN LINEAR CONDENSATION POLYMERS *24*

3-1. Statement of the problem and definitions..... 24
3-2. Mathematical development..... 26
3-3. Applications..... 29
Problems..... 31

4. FUNDAMENTALS OF STATISTICAL MECHANICS: PROBABILITY EQUATION OF THE MOST PROBABLE STATE *32*

4-1. Introduction..... 32
4-2. Types and magnitudes of energies possessed by molecules 33
4-3. The population of energy states..... 38
4-4. The probability of different distributions and the conditions for the maximum probability..... 41
4-5. The probability of fluctuations from the distribution of the most probable state..... 44
Problems..... 46

5. Derivation and Significance of the Boltzmann Distribution Law 48

5-1. Derivation of the Boltzmann equation by the method of undetermined multipliers ..... 48
5-2. Evaluation of the constant $\alpha$ ..... 50
5-3. The partition function ..... 51
5-4. Definition of average values in statistical thermodynamics ..... 52
5-5. The average translational energy and the significance of the constant $\beta$ ..... 53
5-6. Quantum derivation of the Boltzmann equation ..... 55
5-7. The Maxwell equation for the distribution of velocities and other forms of the Boltzmann equation ..... 57
5-8. Average velocities ..... 60
Problems ..... 61

6. Interionic Attraction Theory of Strong Electrolytes 62

6-1. Statement and thermodynamics of the problem and outline of the theoretical method to be followed .... 62
6-2. Mathematical derivation of the limiting law ..... 66
6-3. The equation for the activity coefficient and test of the theory ..... 75
6-4. Extensions of the limiting law ..... 77
6-5. Statistical theory of ion association ..... 77
Problems ..... 80

7. Relation of Thermodynamic Functions to the Partition Function 81

7-1. The total energy and the partition function ..... 81
7-2. Work and the partition function ..... 83
7-3. Heat and the partition function ..... 85
7-4. Entropy and the partition function: the introduction of the absolute temperature ..... 86
7-5. Entropy and probability ..... 87
7-6. Thermodynamic functions in terms of the partition function ..... 90
Problems ..... 92

8. PRELIMINARY CONSIDERATIONS IN EVALUATION OF THE PARTITION FUNCTION *93*

8-1. Separation of the partition function according to energy type ..... 93
8-2. Moments of inertia, symmetry numbers, and the reduced mass ..... 95
8-3. The linear harmonic oscillator and the statistical weight 98
8-4. The Schrödinger wave equation ..... 101
Problems ..... 104

9. EVALUATION OF TRANSLATIONAL, ROTATIONAL, AND VIBRATIONAL PARTITION FUNCTIONS FOR PERFECT GASES *105*

9-1. The translational partition function ..... 105
9-2. Translational contributions to thermodynamic functions 108
9-3. The rotational partition function ..... 108
9-4. The vibrational partition function ..... 113
9-5. Rotational and vibrational contributions to thermodynamic functions ..... 114
9-6. Electronic partition function and the partition function factor for the energy zero ..... 116
9-7. Additional problems in the evaluation of partition functions ..... 120
Problems ..... 122

10. HEAT CAPACITY OF GASES AND SOLIDS *124*

10-1. Rotational partition functions for ortho- and para-hydrogen and deuterium ..... 124
10-2. Heat capacity of hydrogen at high temperatures ..... 131
10-3. Heat capacity of diatomic gases ..... 132
10-4. Heat capacity of polyatomic gases ..... 135
10-5. The specific heat theory of Einstein for solids ..... 138
10-6. Debye's theory of the specific heat of solids ..... 143
10-7. Some special aspects of the specific heats of solids at low temperature ..... 150
Problems ..... 157

11. CALCULATION OF EQUILIBRIUM CONSTANTS IN TERMS OF PARTITION FUNCTIONS *159*

11-1. Thermodynamic relations between free energy, equilibrium constants, and partition functions ..... 159

11-2. Calculations of isotopic exchange equilibrium constants ..... 163
11-3. The problem of internal rotation ..... 170
11-4. Detailed calculation of a chemical equilibrium constant ..... 175
Problems ..... 181

12. Entropy of Chemical Substances *183*

12-1. The entropy of hydrogen ..... 183
12-2. The entropy of water and other inorganic compounds 186
12-3. The entropy of ethane and other hydrocarbons ..... 188
12-4. Corrections to the entropy for nonideal gas behavior 190
Problems ..... 193

13. Statistical Thermodynamics of Adsorption *194*

13-1. Ideal mobile monolayer adsorption ..... 194
13-2. Ideal localized monolayer adsorption ..... 195
13-3. Ideal localized multilayer adsorption ..... 196
Problems ..... 204

14. Bose-Einstein and Fermi-Dirac Statistics *206*

14-1. Introduction ..... 206
14-2. The Bose-Einstein statistics ..... 207
14-3. The Fermi-Dirac statistics ..... 211
Problems ..... 215

Appendix *217*

*Table 1*: Values of Useful Constants ..... 219
*Table 2*: International Atomic Weights ..... 220
*Table 3*: Some Isotopic Masses and Spins ..... 221
*Table 4*: Conversion Factors for Units of Molecular Energy ..... 222
*Table 5*: A Six-Place Table of the Einstein Functions 223
*Table 6*: *G* Function of Bigeleisen and Mayer ..... 240
*Table 7*: Some Useful Integrals ..... 242

Index *242*

# INTRODUCTION TO
# STATISTICAL
# THERMODYNAMICS

# *Chapter 1*

# INTRODUCTION

1-1. The Fundamental Basis of Thermodynamics. 1-2. The Fundamental Basis of Statistical Mechanics. 1-3. Statistical Thermodynamics and Its Relation to Statistical Mechanics and Thermodynamics.

## 1-1. *The fundamental basis of thermodynamics*

Thermodynamics is based on three great laws, which in popular and qualitative language may be stated by saying: first, that it is impossible to build a macroscopic perpetual motion machine of the first class (law of the conservation of energy); second, that it is impossible to build a perpetual motion machine of the second class (one that converts heat from some great reservoir such as the ocean into work at constant temperature); and third, that it is impossible to build a machine or to devise an operation by which the absolute zero of temperature can be attained. These laws[1] can be expressed in mathematical form, and from them it is possible to derive many relations of great theoretical and practical interest. Such equations will be exact; in fact, thermodynamics, insofar as macroscopic systems and phenomena are concerned, may be said to constitute an exact science. Tolman[2] in 1926 declared: "We must regard the theorems of thermodynamics as among the most certain possessions of science." Nothing has happened since then to change the validity of these theorems. As stated above, the three fundamental laws of thermodynamics are valid even for nuclear processes.

Thermodynamics deals with external variables such as mass, pressure, volume, temperature, and heat.

In thermodynamics we do not inquire into the atomic nature of

[1] See, for example, I. M. Klotz, *Chemical Thermodynamics*, Prentice-Hall, Inc., New York, 1950.

[2] R. C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, Chemical Catalog Co., New York, 1927, p. 20.

matter; nor is the validity of its equations dependent on the validity of the atomic and molecular theory or of kinetic theory. It would be possible to establish a whole thermodynamic system in terms of mass instead of moles if we so wished, and as a matter of fact, this is just what Gibbs[3] did in his early thermodynamic work in 1876 at a time when atomic and molecular weights were not known with precision.

However, the very generality of thermodynamics limits it in its theorems, predictions, and applications. For example, although thermodynamics tells us how to define an equilibrium constant for the reaction

$$CO_2^{16}\,(g) + 2H_2O^{18}\,(l) \rightleftarrows CO_2^{18}\,(g) + 2H_2O^{16}\,(l)$$

without experimental determination of empirical parameters, it cannot tell us whether or not $K$ will differ from unity. Thermodynamics tells us how to define and to measure the entropy of a mole of argon in its standard state at 25°C, but from thermodynamics alone we have no way of calculating theoretically its absolute magnitude. The inability of thermodynamics to solve problems of kinetics is too well known to belabor here.

When the chemical system under investigation contains a very small number of particles or of gas molecules as in a dilute colloidal dispersion or in a gas at an amazingly low pressure (as exists for example, in interstellar space), we find that the concentration or pressure at any designated location begins to fluctuate, and then we have to consider the probability that at any moment the pressure or concentration will have this or that value. Our thermodynamic theorems then become subject to probability considerations, and it becomes more logical to develop theorems pertaining to such systems from the standpoint of the principles of statistical mechanics.

## 1-2. *The fundamental basis of statistical mechanics*

In contrast to thermodynamics, statistical mechanics accepts at the outset the atomic-molecular theory and point of view. Adopting the laws of mechanics, it considers the molecule as a dynamical body to which a velocity and momentum in a definite direction may

[3] J. W. Gibbs, *Collected Works*, Longmans, Green & Co., Inc., New York, 1928, Vol. 1, p. 55.

be assigned, as well as a specific location in space (subject to the limitations imposed by the quantum mechanics). From the laws of ordinary mechanics it should be possible to predict at some later instant the position and velocity of a particle if the latter are known at time zero. However, in a gaseous system that contains millions and millions of molecules ($1.14 \times 10^{13}$ molecules per cubic centimeter at $10^{-6}$ mm. Hg and at 25°C), calculation of the precise behavior of all of these molecules becomes prohibitively complicated and impossible, so that statistical methods have to be employed. The average behavior can quite exactly be calculated, as we shall see in later sections of this book; and it is this average behavior that interests us from the standpoint of predicting observable properties.

Statistical mechanics may be said to be the science that enables us to make reasonable predictions of the future average behavior of a system (by system we mean a collection of molecules), starting with a knowledge that does not include a complete description of the condition of each molecule.

Statistical mechanics begins by assigning to each particle so-called generalized coordinates $q_1 \ldots q_f$ and generalized momenta, $p_1 \ldots p_f$. For each monatomic gas molecule in a gaseous system and in its electronic ground state it is sufficient to assign three coordinates $x$, $y$, $z$ and three conjugate momenta $p_x$, $p_y$, $p_z$. The momenta are called conjugate when they are related to the coordinates by the equations of motion in the so-called Hamiltonian or canonical form

$$\frac{\partial H}{\partial p_i} = \frac{\partial q_i}{\partial t} = \dot{q}_i \tag{1.2.1}$$

$$\frac{\partial H}{\partial q_i} = -\frac{\partial p_i}{\partial t} = -\dot{p}_i \tag{1.2.2}$$

where $t$ represents time. In the absence of a potential energy, the Hamiltonian function $H$ is equal to the total kinetic energy of the system.[4]

The state of a system can be described (not completely) by plotting one point for each molecule in a space of six dimensions. Such a space is called phase space and in general has ($q_1 \ldots q_f$) plus

[4] In R. C. Tolman's comprehensive book, *The Principles of Statistical Mechanics*, Oxford University Press, New York, 1938, the student will find an extensive description of the fundamentals of statistical mechanics. Chap. 2 contains the elements of classical mechanics.

($p_1$ . . . $p_f$) or $2f$ dimensions, where $f$ is the number of degrees of freedom (3 for a monatomic gas) per molecule. If one point in such a space represents all the generalized coordinates and momenta of $N$ particles so that the space has $2Nf$ dimensions, it is called $\gamma$-space, but if it has $2f$ dimensions as described above, it is called $\mu$-space.[5] We shall restrict ourselves chiefly to the use of $\mu$-space of six dimensions, although at one point later in the book it will be convenient to make use of a phase space with only two dimensions, $q$ and $p$.

There are several deeply significant reasons for choosing $q$ and $p$ as the dimensions rather than $q$ and the velocity $v$, let us say. Possibly the most significant reason is one that was entirely unforeseen by the early masters of statistical mechanics such as Maxwell, Boltzmann, and Gibbs. This is that the product of the least error in determining $q$ and $p$ has the order of magnitude and physical dimensions (action) of Planck's constant $h$, or

$$\Delta p \, \Delta q \simeq h \tag{1.2.3}$$

Equation (1.2.3) is the mathematical expression of Heisenberg's uncertainty principle,[6] and with it we shall be able to demonstrate later in this book that the smallest volume of physical significance in $\mu$-space is $h^3$. Thus the use of $q$ and $p$ enables us to fix the size of the unit cell in phase space.

By the use of the generalized coordinates and momenta as the dimensions of phase space it is possible to derive Liouville's theorem, which states that if we follow a moving particle in phase space, the density of particles at that point does not change with time. This derivation involves the use of Eqs. (1.2.1) and (1.2.2), which contain the coordinates and momenta and not the coordinates and velocities. Furthermore, the change of scale of the coordinates does not affect the volume of phase space provided that the scales of energy and time are not changed.

When we hunt for a particular point representing a particle in phase space and look at a particular section of the volume, it is reasonable to believe that the larger the volume, the greater the

[5] For a description of phase space, see R. C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, Chemical Catalog Co., New York, 1927, p. 32.

[6] For a recent description of this principle see K. S. Pitzer, *Quantum Chemistry*, Prentice-Hall, Inc., New York, 1953, p. 14.

probability of finding the point in that particular volume. We come now to one of the fundamental postulates of statistical mechanics, which seems reasonable but which can be justified only by agreement of ultimate calculations with observation. This postulate is the hypothesis of equal a priori probabilities for different regions of phase space. For example, if a point representing the particle passes through various regions of phase space over a long period of time, at any moment it will be equally likely to find that point in any one of these regions as in any other. The time average of a property over the motion of the system can be replaced by the volume average.

If we can imagine a region of $\gamma$-space whose points represent systems with total energy within the range $E$ and $E + \Delta E$, and imagine this region divided into small elements of volume $dq_1 \ldots dp_{nf}$, then each of these different microscopic regions has the same probability. A point representing a system at any random time has an equal chance of being in any of the microscopic regions through which it actually passes during a long period of time. The combined probability of the microscopic regions in which the points representing the systems find themselves will be proportional to the total volume of phase space containing the points. Useful averages of a property can be obtained by summing the values of the property corresponding to all its microscopic states and dividing by the number of such states in the energy range concerned.

The above statements can be expressed mathematically by the following equations: If we let $W$ represent the integral over phase space for which the energy lies between $E$ and $E + \Delta E$,

$$W(t) = \int \ldots \int dp_1 \ldots dq_{nf} \tag{1.2.4}$$

then the Liouville theorem requires that[7]

$$\frac{dW}{dt} = 0 \tag{1.2.5}$$

If at or near the location of one moving point $\rho$ represents the density with which representative points of an ensemble are distributed in phase space, $\rho$ will be a function of the $2nf$ coordinates and

[7] See J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, Inc., New York, 1940, p. 61.

momenta and of the time

$$\rho = \rho(q,p,t)$$

and Liouville's theorem can be expressed in the form

$$\frac{d\rho}{dt} = 0 \tag{1.2.6}$$

If $N$ is the total number of systems under consideration, or the total number of points representing these systems distributed in phase space,

$$N = \int \ldots \int \rho(q,p,t)dq_1 \ldots dp_{nf} \tag{1.2.7}$$

where the integration is taken over the whole of phase space, or

$$N = \int \rho \, dW \tag{1.2.8}$$

Suppose $F(q,p)$ represents some property of a system that is a function of $q$ and $p$. We can define an average value of $F$, $\bar{F}(q,p)$ by the equation[8]

$$\bar{F}(q,p) = \frac{1}{N}\int \ldots \int F(q,p)\rho(q,p,t)dq_1 \ldots dp_{nf} \tag{1.2.9}$$

or

$$\bar{F}(q,p) = \frac{\int \ldots \int F(q,p)\rho(q,p,t)dq_1 \ldots dp_{nf}}{\int \ldots \int \rho(q,p,t)dq_1 \ldots dp_{nf}} \tag{1.2.10}$$

Thus, phase space is useful to us in the determination of averages, and it is these averages that will be correlated with thermodynamic properties. Many actual examples of the calculation of averages will be given in later chapters.

Phase space will also be useful in the estimation of an important function called the partition function. This function is the particular statistical mechanical quantity through which thermodynamic functions such as the energy, free energy, and entropy can most conveniently be expressed in terms of the intrinsic properties of molecules. In fact, we can say that the major purpose of this book is the derivation, evaluation, and application of the partition function to systems of chemical interest. Partition functions based on

[8] R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, New York, 1938, p. 47 ($\gamma$-space) and p. 91 ($\mu$-space).

classical theory are given by the integral of the Boltzmann factor over all of phase space, divided by $h^f$. The division by $h^f$ makes the partition function dimensionless, so that the partition function is always a pure number. The Boltzmann factor is derived and discussed in Chapter 5.

The development of statistical mechanics begins with calculation of the probability of a particular distribution of points among the unit cells or volume elements of phase space. Then the distribution having the maximum probability is found, and from this distribution average properties can be calculated that will not change with time. These averages will represent equilibrium properties of the system. The calculation of the probability of a slight fluctuation, say of the order of magnitude of 0.1%, from the distribution of maximum probability demonstrates that if the number of particles per cubic centimeter is large, such fluctuations are overwhelmingly improbable. From the differential equation corresponding to the most probable state and the conditions of constant total energy and total number of particles the Boltzmann distribution law is derived. It is possible to derive laws for other types of distributions, depending on the type of postulate concerning the distribution of points in phase space (Chapter 14).

The partition function follows easily and logically from the development of the Boltzmann equation and the evaluation of its constants of integration.

## 1-3. *Statistical thermodynamics and its relation to statistical mechanics and thermodynamics*

Statistical thermodynamics is the science that deals with application of the postulates, theorems, and methods of statistical classical mechanics and statistical quantum mechanics to the description, understanding, and solution of thermodynamic problems. In particular, statistical thermodynamics makes use of the partition function of statistical mechanics, because, by means of it, average values of the energy or of other properties of the system can be defined and calculated.

Inasmuch as the numerical value of the partition function is calculated by making use of intrinsic information pertaining to atoms and molecules, it is possible to calculate thermodynamic functions from these facts and to relate the external variables of

thermodynamics to the internal properties of molecules. This observable or experimentally derivable intrinsic information includes data for atomic masses, internuclear distances, bond angles, moments of inertia, vibrational frequencies, electronic energy values, symmetry numbers, statistical weights, etc. All of these constitute a vast body of facts from which the detailed calculations of statistical thermodynamics are made.

Statistical thermodynamics in principle does not have the rigor and exactness of thermodynamics (although it may be more accurate in actual practice), and there is really no a priori method of proving the validity of the postulates of statistical mechanics on which statistical thermodynamics is based. The justification for this science and the validity of its calculations are found in the agreement of its calculations and predictions with observation. Despite this lack of rigor we find that the study of statistical thermodynamics gives us a beautiful understanding of the laws of thermodynamics in terms of the properties of individual molecules; it enables us to predict the exact values of specific heats, entropies, free energy changes, equilibrium constants of many systems and reactions. Furthermore, the methods used are applicable in part to the study of kinetics and the rate of approach to equilibrium, so that statistical thermodynamics serves as a good foundation from which to begin a theoretical interpretation of reaction rates and fluctuations from the equilibrium state.

Just as thermodynamics has certain limitations, so does statistical thermodynamics. The limitations are not of principle, once the initial postulates have been accepted, but of practical applications, particularly in the case of large and complicated molecules, gases at high pressure, condensed systems such as liquids and concentrated solutions. In large and complicated molecules there are many different vibrational frequencies whose fundamental modes must be known. Furthermore, the vibrations will not be of the ideal linear harmonic type, which means that anharmonicity correction factors will have to be estimated. The rotation of the molceule will likewise not be capable of simple mathematical description, but internal rotations or oscillations will have to be considered and stretching factors determined. In condensed systems like liquids and gases at high pressure, the potential energy of the molecules becomes a (mostly unknown) function of position, making the

integration of the Boltzmann factor over phase space very difficult mathematically if not entirely impossible.

Despite the difficulties in treating large molecules and condensed systems, considerable progress has been made, and much activity in this field is now evident. Statistical methods have in the last 20 years been usefully and brilliantly applied to many systems of chemical interest. For certain simple molecules the partition functions are now known so accurately that we can probably calculate many properties such as specific heats, entropies, and equilibrium constants more precisely than they can be measured. The effect of nuclear spin and isotopic composition can easily and logically be taken into account. The theory of solutions, including strong electrolytes, has been greatly advanced by statistical methods (use of the Boltzmann equation, particularly). In the field of high polymers, a field of particular interest to organic chemists, application of statistical methods has been especially useful. A new brand of science, biophysical chemistry, with the statistical approach serving as one of its fundamental methods, has been created largely since the end of the second world war. In 1926 Tolman stated: "More and more the chemist must turn to the methods of statistical mechanics in order to continue the theoretical development of his science."[9] In accordance with his prediction, the chemist has turned to statistical methods, and by combining them with the methods of thermodynamics, has evolved the science of statistical thermodynamics, a science described by Schrödinger[10] as "conceptionally so enormously difficult."

[9] R. C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, Chemical Catalog Co., New York, 1927, p. 18.

[10] E. Schrödinger, *Statistical Thermodynamics*, 2d ed., Cambridge University Press, London, 1952, p. 42.

# *Chapter 2*

# INTRODUCTION TO MATHEMATICAL PROBABILITY

2-1. Definitions: Mathematical Probability. 2-2. The Theorems of Total and Compound Probability. 2-3. Permutations, Combinations, Complexions, Examples. 2-4. The Problem of Repeated Trials, Binomial Theorem, A Priori Probability, Statistical Weight. 2-5. Properties of Factorials.

## 2-1. *Definitions: mathematical probability*

The words "necessity, chance, probability" suggest to all of us certain concepts and ideas, with which we are qualitatively familiar, but with which the average student of chemistry has not been given any precise knowledge.

Mathematical probability may be defined in the following way:[1]

> *If, consistent with conditions S, there are n exhaustive, mutually exclusive, and equally likely cases, and m of them are favorable to an event A, then the mathematical probability of A is defined as the ratio m/n.*

For two events to be equally likely, or equally probable, it is necessary that "after taking into consideration all relevant evidence, one of them cannot be expected in preference to the other."[2] For example, in the single toss of a perfectly balanced cubic die, it cannot be expected that the die will come to rest on any one of its six sides with preference to the other; in other words, any one of the numbers from one to six on the die has an equal chance of coming up. The proof of the equal likelihood of all six ways in which the die can come to rest can easily be gained experimentally by tossing the

[1] J. V. Uspensky, *Introduction to Mathematical Probability*, McGraw-Hill Book Co., Inc., New York, 1937, p. 6.

[2] *Ibid.*, p. 5.

die a great number of times and recording the number of times each of the six numbers appears on top. These numbers should all be very nearly equal, and indeed closer to each other, the larger the number of tosses.

The appearance of any of the numbers on the die represents a mutually exclusive case, because obviously two numbers cannot appear at the same time; furthermore, the events one to six are exhaustive inasmuch as there are six and only six ways in which the die can come to rest.

As an example of the application of the above mathematical definition of probability, let us consider the probability of obtaining four as the number on the top face of the die in a single toss; this will be called event $A$ of the definition. Now there are six mutually exclusive and equally likely cases or ways in which the die will come to rest because of the six sides of the die, $n$ equal to 6, but only one gives the result we want, namely, a four on the top face, $m$ equal to 1; hence the mathematical probability of the number four coming up is 1/6. Similarly the chance of obtaining any of the other numbers is also 1/6. Since there are only six sides to the die and since the probability of each appearing on top is 1/6, the total probability of all added together is unity; this serves as a definition of complete certainty. The maximum probability that any event can have is unity by the definition given above and this corresponds to complete certainty. Similarly, if there are no cases favorable to the event $A$, and $m$ equal to zero, the probability of the event $A$ is zero, and it is an impossibility.

## 2-2. *The theorems of total and compound probability*

*The total probability*[3] *of an event A is the sum of the probabilities of its mutually exclusive forms,* $A_1, A_2, \ldots, A_n$.

Consider the probability of obtaining a total of 7 points on the toss of two dice. There are six mutually exclusive ways in which 7 can be obtained:

| | | | | | | |
|---|---|---|---|---|---|---|
| *First die:* | 1 | 2 | 3 | 4 | 5 | 6 |
| *Second die:* | 6 | 5 | 4 | 3 | 2 | 1 |

These cases are mutually exclusive because when a seven has come

[3] *Ibid.*, p. 28.

up in any of the above six ways, it obviously cannot be obtained in any of the other ways in this single toss of the two dice. Now the probability of obtaining a seven according to the first combination listed above, namely by throwing a one and a six, is only 1/36 because there is only one way in which a one on one die and a six on the second die can occur. But there are a total of 36 ways in which all numbers on both dice can appear, i.e., 36 mutually exclusive and equally likely ways in which two dice will come to rest after a toss; hence the probability of throwing two dice so that a one comes up on the first die and a six on the second is 1/36. Similarly, the probability of each of the cases listed above is 1/36, and as there are six of them favorable to obtaining a seven, the total probability of getting a seven is 6/36 or 1/6.

Of equal importance with the theorem of total probability is the theorem of compound probability which may be stated as follows:

> *The probability of the simultaneous occurrence of A and B is given by the product of the unconditional probability of the event A by the conditional probability of B, supposing that A actually occurred.*[4]

If we let $W_A$ be the mathematical probability of $A$, $W_B$ that of $B$ (after $A$ has occurred), and $W_{AB}$ that of simultaneous occurrence of $A$ and $B$, then

$$W_A W_B = W_{AB} \tag{2.2.1}$$

In the example above of tossing two dice so that 1 comes up on the first die and the 6 on the second, the probability of each event is 1/6, so by the theorem of compound probability, the probability of getting both a 1 and a 6 simultaneously from the two dice is (1/6)(1/6) or 1/36.

We can illustrate the theorems of total and compound probability by the following problem:

An urn contains 2 white and 3 black balls, all balls being indistinguishable except for their colors. Three balls are drawn from the urn; what is the probability that the third ball is white? Letting $B$ represent the draw of a black ball and $W$ that of a white, we can list all possible ways in which three balls can be drawn in any sequence ending with a white ball on the third draw.

[4] *Ibid.*, p. 31.

$$\begin{aligned} B - W - W \quad & \tfrac{3}{5} \cdot \tfrac{2}{4} \cdot \tfrac{1}{3} = \tfrac{1}{10} \\ W - B - W \quad & \tfrac{2}{5} \cdot \tfrac{3}{4} \cdot \tfrac{1}{3} = \tfrac{1}{10} \\ B - B - W \quad & \tfrac{3}{5} \cdot \tfrac{2}{4} \cdot \tfrac{2}{3} = \tfrac{2}{10} \\ \text{Total probability} \quad & = \tfrac{2}{5} \end{aligned}$$

Beside the listing of the sequence with which the balls were drawn there is given the probability of each draw. The probability of each sequence is the product of the probability of each of the three draws, and the total probability of drawing a white ball on the third draw is the sum of the probabilities of each sequence of draws, or 2/5.

## 2-3. *Permutations, combinations, complexions, examples*

In physical problems it is frequently necessary to know the number of ways a certain number of objects can be arranged into various configurations. We begin with the development of an equation for the number of permutations, $P_n$ of $n$ objects, or number of ways in which $n$ objects can be placed in different orders. For example, suppose we consider 4 objects distinguished by the letters

$$a - b - c - d$$

There are four ways in which these letters may be written down in a linear array so that first $a$, then $b$, $c$, and $d$ begin the sequence. For each of these four ways of starting the sequence, there are three more in which the second letter can be chosen, inasmuch as after choosing the first letter there are three letters left. For each of the 12 ways of choosing or arranging the first two, there are two ways of choosing the third letter but only one way for the last, since when three letters have been written down, only one is left. The total number of permutations is therefore given by the product

$$4 \cdot 3 \cdot 2 \cdot 1 = 4!$$

In general we can say that the total number of permutations $P_n$ is simply equal to $n!$ A number with an exclamation point after it, such as $n!$, is called $n$ factorial and is the product of all integers from 1 to $n$ to and including $n$, or

$$n! = (1)(2)(3)(4) \ . \ . \ . \ (n-2)(n-1)n \qquad (2.3.1)$$

Various properties of factorials are reviewed at the end of this chapter.

Another number of interest to us is the number of ways of drawing $m$ objects out of $n$, or of arranging $n$ objects taken $m$ at a time. This number is designated by the symbol $A_n{}^m$. Suppose we pick two letters out of the four listed above, and enumerate all possible ways of doing this. There are four ways in which the first letter may be chosen, and for each of these four ways of choosing the first letter, there are three more of choosing the second; hence there are twelve ways in which any two letters may be picked out of the four, and listed:

| | | |
|---|---|---|
| $ab$ | $ac$ | $ad$ |
| $ba$ | $bc$ | $bd$ |
| $ca$ | $cb$ | $cd$ |
| $da$ | $db$ | $dc$ |

This number of arrangements of $n$ objects taken $m$ at a time is given by the expression

$$A_n{}^m = n(n-1)(n-2) \ldots (n-m+1) \qquad (2.3.2)$$

A mathematically equivalent way of writing Eq. (2.3.2) is obtained by multiplying (2.3.2) by

$$\frac{(n-m)!}{(n-m)!}$$

But $(n)(n-1)(n-2) \ldots (n-m+1)[(n-m)!] = n!$; hence (2.3.2) becomes

$$A_n{}^m = \frac{n!}{(n-m)!} \qquad (2.3.3)$$

Now this method of arranging the objects takes into account the order of such arrangements, i.e., the arrangement $ab$ is distinguished from $ba$. If we wish to know the number of arrangements of $n$ objects taken $m$ at a time, not taking into account the order, which is called the number of combinations or complexions, we must divide (2.3.3) by $m!$, since ignoring the order reduces the number of arrangements by the factor equal to just the number of ways $m$ objects can be permuted. Letting $C_n{}^m$ be the number of combinations or complexions of $n$ objects taken $m$ at a time, we have

$$C_n{}^m = \frac{n!}{(n-m)!m!} \qquad (2.3.4)$$

Equation (2.3.4) is the definition, therefore, of the number of combinations or complexions. In the example given above, if we eliminate all duplicating terms, such as *ba* which duplicates *ab* (neglecting the order), we have

*ab* *ac* *ad*
*bc* *bd*
*cd*

or six, which is equal to

$$\frac{4!}{2!2!}$$

in agreement with (2.3.4).

The use of (2.3.4) in probability calculations can be illustrated by the following problem: An urn contains 3 white and 5 black balls. Five balls are drawn at random. What is the probability of drawing 2 white and 3 black balls? The number of ways 2 white balls can be drawn out of 3 white balls is $C_3^2$ (not taking into account order) or

$$\frac{3!}{2!1!}$$

The number of ways 3 black balls can be drawn out of 5 black is

$$\frac{5!}{3!2!}$$

The total number of ways this combination of white and black balls can be drawn is

$$\frac{3!}{2!1!} \cdot \frac{5!}{3!2!}$$

The total number of ways five balls can be drawn out of eight without regard to color is

$$\frac{8!}{5!3!}$$

Hence the probability of drawing 2 white and 3 black balls out of the 3 white and 5 black balls is

$$\frac{\frac{3!}{2!1!} \cdot \frac{5!}{3!2!}}{\frac{8!}{5!3!}}$$

or 15/28.

Equation (2.3.4) can be generalized to cover the case of drawing $m_1, m_2, m_3$ objects out of a total of $n$ (this generalization is one of the problems at the end of the chapter); the result is

$$C_n^{m_1,m_2,m_3\cdots} = \frac{n!}{m_1!m_2!m_3!\ \ldots} \tag{2.3.5}$$

Equation (2.3.5) will turn out to be of considerable importance in the development of the Boltzmann distribution law.

Other equations for the number of combinations or complexions of special systems can be written. For example, one expression that has many important applications in physical science is

$$C_1 = \frac{S!}{(S - n_1)!n_1!} \tag{2.3.6}$$

This equation gives the total number of *distinguishable* ways in which $n_1$ *indistinguishable* balls can be dropped into $S$ *distinguishable* boxes, there being allowed only one ball to a box. The condition of distinguishability or indistinguishability is important, because the number of complexions or combinations is greatly altered if distinguishable objects become indistinguishable. Thus, if we have three boxes distinguished by the numbers one to three, and drop into them at random a white ball and a black ball, the following complexions are distinguishable and significant:

| *Box No.:* | *1* | *2* | *3* | *Complexion No.* |
|---|---|---|---|---|
| | [ *W* ] | [ *B* ] | [ ] | 1 |
| | [ *W* ] | [ ] | [ *B* ] | 2 |
| | [ ] | [ *W* ] | [ *B* ] | 3 |
| | [ *B* ] | [ *W* ] | [ ] | 4 |
| | [ *B* ] | [ ] | [ *W* ] | 5 |
| | [ ] | [ *B* ] | [ *W* ] | 6 |
| | [*WB*] | [ ] | [ ] | 7 |
| | [ ] | [*WB*] | [ ] | 8 |
| | [ ] | [ ] | [*WB*] | 9 |

If we adopt the condition that there may be only one ball in a box, complexions 7, 8, and 9 have to be eliminated; if we adopt the condition that the balls are indistinguishable, complexion 1 becomes identical with 4, 2 with 5, 3 with 6, leaving only 3 complexions to be counted. As far as applications to physical science are concerned, it is the case of nondistinguishability of the balls that interests us

most, because the balls essentially represent molecules, and the molecules of any one compound are physically indistinguishable.

Equation (2.3.6) tells us therefore the number of physically distinguishable ways $n_1$ molecules can be distributed on $S$ sites to the depth of a one molecular layer (one monolayer). Thus Eq. (2.3.6) is of importance in adsorption theory. It has also been used to compute the number of ways $y$ side chains can be distributed at random on $S$ carbon atoms of the main chain in a paraffinic hydrocarbon containing branched chains.[5] Equation (2.3.6) is used in the derivation of the Fermi-Dirac distribution function where only one particle per energy (quantum) state is allowed. Equations for other combinatory problems are involved in the problems given at the end of the chapter.

## 2-4. *The problem of repeated trials, binomial theorem, a priori probability, statistical weight*

Among the problems of probability calculations, the problems of the so-called repeated trials have considerable importance. By trial is meant any event such as tossing a coin or die, drawing a card at random, or dropping a number of balls into various boxes. Let us now assume that each trial can be classified as a success or a failure; for example, in tossing a coin we may define the coming up of a head as a success and that of a tail as a failure. If we let $p$ represent the probability of a success and $q$ the probability of a failure, then it is necessary that

$$p + q = 1 \tag{2.4.1}$$

because it is a certainty (probability equal to unity) that the trial be a success or failure. If we let $n$ be the number of trials, the probability that all $n$ trials are successes is $p^n$, and the probability that all $n$ trials are failures is $q^n$; also

$$q^n = (1 - p)^n$$

The probability $W$ that out of $n$ trials there are $m$ successes and $n - m$ failures is given by the expression

$$W = \frac{n!}{(n - m)!m!} p^m q^{n-m} \tag{2.4.2}$$

[5] M. Dole, W. P. Hettinger, Jr., N. R. Larson, and J. A. Wethington, Jr. *J. Chem. Phys.*, **20,** 781 (1952).

Equation (2.4.2) arises from the fact that the second part of the equation, the multiplicand $p^m q^{n-m}$, is the probability of gaining $m$ successes and $n - m$ failures *just one way*, while the multiplying factor or multiplier

$$\frac{n!}{(n-m)!m!}$$

is the number of ways $n$ trials may be carried out so as to produce $m$ successes and $(n - m)$ failures. For example, if a coin is tossed five times, the probability of getting heads three times and tails twice in one and only one particular sequence is $(1/2)^3 \cdot (1/2)^2$ or 1/32, but 3 heads and 2 tails can come up in 10 different ways as predicted by the calculation

$$\frac{5!}{3!2!} = 10$$

All 10 possible sequences of 3 heads and 2 tails can be listed as follows:

*hhhtt*
*hhtht*
*hhtth*
*hthht*
*hthth*
*htthh*
*thhht*
*thhth*
*tthhh*

Thus the total probability that 3 heads and 2 tails will come up on five tosses of a coin in any sequence whatever is 10/32.

The symbol $p$ is called the a priori probability of a success and $q$ the a priori probability of a failure. In the case of an unweighted coin the a priori probability of getting either a head or a tail is 1/2.

If we have $n$ tosses of a coin, all possible combinations of heads or tails can be expressed by $(p + q)$ raised to the $n$th power, for example in 3 tosses:

$$(p+q)^3 = p^3 + 3p^2q + 3pq^2 + q^3 \qquad (2.4.3)$$

The exponent of each $p$ and $q$ symbol is equal to the number of times heads or tails has come up for the particular combination of heads

and tails represented by each term of (2.4.3), and the sum of the exponents in each term is equal to 3, or to the number of trials, $n$. The number of terms of (2.4.3) is equal to the number of different combinations of heads and tails that are possible, four in the above example, and the coefficient of each term is equal to the number of ways that particular combination can occur. Thus the combination or sequence of 3 heads can result only in one way, 2 heads and 1 tail in 3 ways, 1 head and 2 tails in 3 ways, and 3 tails in one way. By the binomial theorem, the coefficient of each term in (2.4.3) is given by the expression:

$$\frac{n!}{(n-m)!m!}$$

where $m$ is the number of successes and $n - m$ is the number of failures in $n$ trials or the exponents of $p$ and $q$, respectively. Correspondingly, the multinomial coefficient, the coefficient of $\prod_i p_i^m$ in the sum $\sum_i p_i$ raised to the power $n$ is

$$\frac{n!}{\prod_{i=1}^{r} m_i!}$$

where $\sum_{i=1}^{r} m_i = n$, the number of trials, and $r$ is the number of members $p_i$ in the sum (2 for tossing a coin, 6 for tossing a die).[6]

The actual probability of any of the sequences represented in (2.4.3) is obtained by substituting 1/2 for both $p$ and $q$, inasmuch as 1/2 is the a priori probability of getting either a head or tail in a single toss of an unweighted coin. Suppose the coin is weighted so that heads come up twice as often as tails; then

$$p = \tfrac{2}{3}, \qquad q = \tfrac{1}{3}$$

[6] The symbol $\prod_{i=1}^{n} x_i$ means the product $(x_1)(x_2) \ldots (x_i) \ldots (x_n)$ of a series of factors, $x_1, x_2, \ldots x_i \ldots x_n$, just as $\sum_{i=1}^{n} x_i$ is the sum $(x_1 + x_2 + \ldots x_n)$ of a series of terms. By the symbol $\prod_i m_i!$ we mean $\prod_i (m_i!)$, not $\left[\prod_i m_i\right]!$

Referring to (2.4.3) and substituting these values of $p$ and $q$ to calculate the probability of getting two tails and one head as represented by the third term of (2.4.3), we obtain

$$3(\tfrac{2}{3})(\tfrac{1}{3})^2 = \tfrac{2}{9}$$

In the case of the unweighted coin the corresponding probability was $3(\frac{1}{2})(\frac{1}{2})^2 = \frac{3}{8}$. For the weighted coin, we can say that the statistical weight, $g$ of getting a head is 2 and that of a tail 1. In general, the probability of any series of events $n$ composed of a number of parts $r$, each of which has the a priori probability $\omega$ is given by the equation

$$\dot{W} = \frac{n!}{\prod_{s=1}^{r} n_s!} \prod_{s=1}^{r} \omega_s^{n_s} \qquad (2.4.4)$$

Equations of the type of (2.4.4) have great importance in the development and applications of statistical thermodynamics. As an example of the application of (2.4.4) to probability calculations, let us consider the probability of obtaining two balls in one box, one ball in the second, and none in the third, when three distinguishable balls are dropped at random into three numbered boxes. The a priori probability of getting a ball in any one box out of the three is 1/3; hence the calculation becomes

$$W = \frac{3!}{2!1!0!}\left(\frac{1}{3}\right)^2\left(\frac{1}{3}\right)^1\left(\frac{1}{3}\right)^0 = \frac{1}{9}$$

The above example concludes our brief introduction to the mathematics of probability. In the next chapter we show how these fundamental concepts of probability can be immediately applied to the solution of a chemical problem of great interest without further development of the principles of statistical thermodynamics, namely, the problem of the distribution of molecular weights in the formation of a linear condensation polymer such as a polyester or polyamide. As Chapter 3 is not essential for the chapters that follow, one may turn directly to Chapter 4 without detriment in the study of statistical thermodynamics.

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## 2-5. *Properties of factorials*

In addition to a factorial number $n!$ being equal to the product of all the integers from one to $n$, a factorial number may also be expressed by the equation

$$n! = \int_0^\infty x^n e^{-x}\, dx \tag{2.5.1}$$

Factorial $n$ is unity for $n$ equal both to unity or to zero. We shall not be concerned in this course with the value of factorial negative numbers. An equation for $n!$ in terms of $n$ is[7]

$$n! = n^n e^{-n}(2\pi n)^{1/2} e^{f(n)} \tag{2.5.2}$$

where
$$\frac{1}{12(n+\frac{1}{2})} < f(n) < \frac{1}{12n}$$

For large values of $n$, the factor $e^{f(n)}$ becomes practically unity, so that (2.5.2) reduces to the following (expressed in logarithmic form):

$$\ln n! = n \ln n - n + \tfrac{1}{2} \ln n + \tfrac{1}{2} \ln 2\pi \tag{2.5.3}$$

If $n$ is very large, only the first two terms on the right side of (2.5.3) need be retained; in this case (2.5.3) becomes

$$\ln n! = n \ln n - n \tag{2.5.4}$$

Equation (2.5.4) is commonly called Stirling's approximation, although (2.5.2) and (2.5.3) are also forms of Stirling's approximation.

## PROBLEMS

**1.** Compute the probability of getting heads 5 times in 5 tosses of a coin.

**2.** Compute the probability of getting heads 3 times and tails twice in the sequence *hhhtt*.

**3.** Compute the probability of getting 3 heads and 2 tails in any sequence.

**4.** What is the probability of getting a head on the sixth toss after heads have been seen to come up five times in a row?

**5.** Compute the probability of throwing a four twice in two throws of a pair of dice, (i.e., a total of four on the two dice on each toss).

[7] Uspensky, *op. cit.*, p. 352.

**6.** An urn contains 3 white and 5 black balls. Suppose one ball is drawn and color *unnoted*, and then a second ball is drawn. What is the probability that the second ball is white?

**7.** In tossing 10 coins what is the probability of getting (a) 5 heads in just one way, (b) 5 heads in any sequence, (c) 5 or more heads?

**8.** In tossing 10 coins that are weighted so that the chance of getting a head in any one toss is twice as great as getting a tail, what is the probability of getting 5 heads in any sequence?

**9.** Five identical and distinguishable balls are dropped at random into three distinguishable boxes. What is the probability that the first box contains 3 balls, the second box 2 balls, and the third box none?

**10.** Repeat the calculation of problem 9 under the conditions that the first box has two compartments, which gives it an a priori probability twice as great as the other two boxes.

**11.** Three cabinets identical in appearance each have two drawers. The first cabinet contains a gold coin in each drawer, the second a silver coin in each drawer, and the third a gold coin in one drawer and a silver coin in the other. Choose one cabinet at random.

(a) What is the probability that it contains coins of different metals?

(b) If one of the drawers is opened, and found to contain a gold coin, what is the probability that the other drawer in the same cabinet contains a silver coin?[8]

**12.** An urn contains five balls labelled $a$, $b$, $c$, $d$, and $e$. What is the probability of drawing three balls in the exact order $a$, $c$, and $e$.

**13.** Consider five molecules of a hydroxy acid. If each monomeric molecule is tagged so as to be distinguishable, in how many ways could the five molecules dimerize (i.e., form two dimers with one monomer unreacted)? In doing this problem, it must be realized that the number of possibilities depends on recognizing or not recognizing the order in which the monomers form each molecule, and the order in which the two dimeric molecules are formed. Calculate the number of possibilities for each possible combination of assumptions.

[8] This problem is discussed by Uspensky, *op. cit.*, p. 17.

**14.** Deduce a formula for the number of ways $n$ distinguishable objects may be placed in $c$ numbered boxes with no restrictions on the number per box.

**15.** Deduce a formula for the number of ways $n$ distinguishable objects may be placed in $c$ numbered boxes with no more than one object to a box, $n \leq c$.

**16.** Deduce a formula for the number of ways $n$ indistinguishable objects may be placed in $c$ numbered boxes with no restrictions on the number per box.[9]

**17.** Deduce a formula for the total number of sequences, $C_\zeta$, having $\zeta$ empty sites in sequence, in all possible configurations when $n$ side chains are distributed on $S$ carbon atoms along the main chain of a single paraffinic molecule with not more than one side chain to a site.[10]

**18.** Prove Eq. (2.3.5).

**19.** Make a graph of the number of ways each possible number can come up on tossing two dice. What do you conclude from the plot?

[9] The solution to problems 14, 15, and 16 may be found in Mayer and Mayer, *Statistical Mechanics*, John Wiley & Sons, Inc., New York, 1940, p. 437.

[10] The solution to this problem is given by Dole *et al.*, *loc. cit.*

# *Chapter 3*

# DISTRIBUTION OF MOLECULAR WEIGHTS IN LINEAR CONDENSATION POLYMERS

3-1. Statement of the Problem and Definitions. 3-2. Mathematical Development. 3-3. Applications.

## 3-1. *Statement of the problem and definitions*

When two bifunctional molecules react so as to form a dimer, as when a dibasic acid reacts with a glycol or diamine according to the reactions

$$\text{HOOCRCOOH} + \text{HOROH} \rightarrow \text{HOOCRCOROH} + \text{H}_2\text{O}$$

$$\text{HOOCRCOOH} + \text{H}_2\text{NRNH}_2 \rightarrow \text{HOOCRC(=O)NRNH}_2 + \text{H}_2\text{O}$$

$$\text{HOOCRCOOH} + \text{H}_2\text{NRNH}_2 \rightarrow \text{HOOCRC(=NH)OH} + \text{H}_2\text{O}$$

the resulting molecule is still bifunctional and can continue to react, forming longer and longer molecules, which eventually become of high enough molecular weight to be considered high polymers. Now if the residue R, consisting of methylene groups, is large enough, say equal to $-(CH_2)_6-$, the functional groups will be so far apart that the reactivity of each is independent of the presence of the other. This means that the reactivity of the functional group will be independent of the length of the molecule. To such a system the principles of mathematical probability can be applied with great accuracy and value.[1] The problem can be stated with the questions: Will each long chain molecule that is formed have exactly the same molecular weight or will one polymeric molecule be longer than

[1] This was first extensively done by P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).

another and will there be a distribution of molecular weights? Will a preponderance of long or short molecules result? Will the greatest fraction by weight of the material be found in the group containing the high or low molecular weights? To what extent should the polymerization be carried to obtain the greatest weight fraction at any desired molecular weight? The application of the methods of mathematical probability of the previous chapter enables us to answer these questions.

Let us first make the following definitions of symbols. In general, $N$ refers to molar quantities; that is, numbers in terms of moles, while $n$ refers to the actual number of molecules.

$N_0$ = total moles of segments in the long chain molecules or the total moles of monomers before polymerization. By segment we mean, therefore, twice the number on the average of the repeating units in the polymer; for example, in a polyester formed from the condensation of ethylene glycol and adipic acid, the repeating unit is

$$\begin{matrix} & & \text{O} & & \text{O} & \\ & & \| & & \| & \\ -\text{C}(\text{CH}_2)_4\text{COCH}_2\text{CH}_2\text{O}- & & & & & \end{matrix}$$

This repeating unit contains two segments of unequal length, but the fact that their length is unequal is usually immaterial to what follows. For simplicity, we shall assume that at the start of the polymerization both the acid and alcohol, or acid and amine, are present in stoichiometrically equivalent proportions.

$x$ = number of segments in a molecule.

$N_x$ = moles of polymer molecules containing $x$ segments per molecule.

$N$ = total moles of polymerized molecules.

$p$ = degree of polymerization defined by the ratio of the number of bonds formed on polymerization to the total number of possible bonds. It is also equal to the probability that a bond is formed.

$w_x$ = weight of polymer molecules containing $x$ segments per molecule.

$\mathrm{N}_x$ = mole or number fraction of molecules containing $x$ segments per molecule; hence

$$\frac{N_x}{N} = \mathrm{N}_x$$

$w_x$ = weight fraction of molecules containing $x$ segments per molecule,

$$= \frac{w_x}{\sum_x w_x} \quad \text{or} \quad w_x = \frac{xN_x}{N_0}$$

This latter expression for the weight fraction is strictly valid for all values of $x$ only when the two types of segments per repeating unit have the same weight, or if the segment weights are different, only when $x$ is an even number. It also neglects the H and OH at the end of each polymeric molecule. With these definitions we can write

$$\sum_{x=1}^{\infty} N_x = N \tag{3.1.1}$$

$$\sum_{x=1}^{\infty} xN_x = N_0 \tag{3.1.2}$$

Actually, it is meaningless to carry the summation of Eqs. (3.1.1) and (3.1.2) to an infinite chain length of molecules, but mathematically it is justified, since the number of such molecules is zero, as it must be for all molecules whose $x$ is greater than $N_0N_a$, where $N_a$ is Avogadro's number. Furthermore, the number of molecules for which $x$ is very large is usually negligible.

It is easy to develop an important relationship between $p$, $N$, and $N_0$. The number of moles of bonds formed is

$$\sum_x (x - 1)N_x$$

while the total possible number of moles of bonds is $N_0$; hence

$$p = \frac{\sum_x (x - 1)N_x}{N_0} = \frac{\sum_x xN_x - \sum_x N_x}{N_0} = 1 - \frac{N}{N_0} \tag{3.1.3}$$

If $p$ is the probability that a bond is formed, then $(1 - p)$ is the probability that a bond is not formed, or

$$(1 - p) = \frac{N}{N_0} \tag{3.1.4}$$

## 3-2. *Mathematical development*

Instead of calculating the most probable distribution of molecular sizes from the standpoint of the building up of long-chain molecules

from monomers, let us approach the problem by considering the reverse process, that of degradation of a single molecule of such a length that it has $N_0N_a$ segments in it. The number of molecules $x$ segments in length formed by degradation, as by hydrolysis, will be equal to the number of all possible ways in which an $x$-mer (a polymeric molecule having $x$ segments per molecule) can form, multiplied by the probability of forming each $x$-mer in just one way. A single long-chain molecule containing $N_0N_a$ segments can break down into an $x$-mer in the following number of ways (in units of moles).

$$\frac{(N_0N_a - x + 1)}{N_a} \tag{3.2.1}$$

To see this, imagine a molecule 10 segments in length

$$\text{—}_{b'}\text{—}_{c'}\text{—}_{d'}\text{—}_{e'}\text{—}\ \text{—}_{a}\text{—}_{b}\text{—}_{c}\text{—}_{d}\text{—}_{e}$$

A molecule six segments in length can be made by breaking the molecule at $a$, or at $b$ and $b'$, $c$ and $c'$, $d$ and $d'$ and $e'$. Thus out of the decamer it is possible to make a hexamer in 5 different ways; this is equal to $(n_0 - x + 1)$, where $n_0$ is the total number of segments in the long molecule before degradation occurs. Since an $x$-mer has $x - 1$ bonds, and since the probability that each bond is made is $p$, simultaneous occurrence of $(x - 1)$ bonds and 2 ends of the molecule where the bonds are *not* made has the compound probability

$$p^{x-1}(1 - p)^2$$

The moles of $x$-mers become, therefore

$$N_x = \left[N_0 - \frac{(x - 1)}{N_a}\right] p^{x-1}(1 - p)^2 \tag{3.2.2}$$

As Avogadro's number is very large compared with $(x - 1)$, this expression simplifies to[2]

$$N_x = N_0p^{x-1}(1 - p)^2 \tag{3.2.3}$$

To obtain the mole fraction of $x$-mers, we divide (3.2.3) by $N$, the total moles of polymeric molecules, making use of (3.1.4).

$$\mathrm{N}_x = \frac{N_x}{N} = \frac{N_0p^{x-1}(1 - p)^2}{N_0(1 - p)}$$

or

$$\mathrm{N}_x = p^{x-1}(1 - p) \tag{3.2.4}$$

[2] Equation (3.2.2) was first given by W. Kuhn, *Ber.*, **63**, 1503 (1930).

The weight fraction of $x$-mers readily follows:

$$w_x = \frac{x_0 N_x}{N_0} = x p^{x-1}(1-p)^2 \tag{3.2.5}$$

The sum of all mole or weight fractions from $x$ equal to unity to $x$ equal to infinity should equal unity. Remembering that

$$\frac{1}{1-p} = 1 + p + p^2 + \cdots$$

and

$$\frac{1}{(1-p)^2} = 1 + 2p + 3p^2 + \cdots$$

the above statement is readily verified.

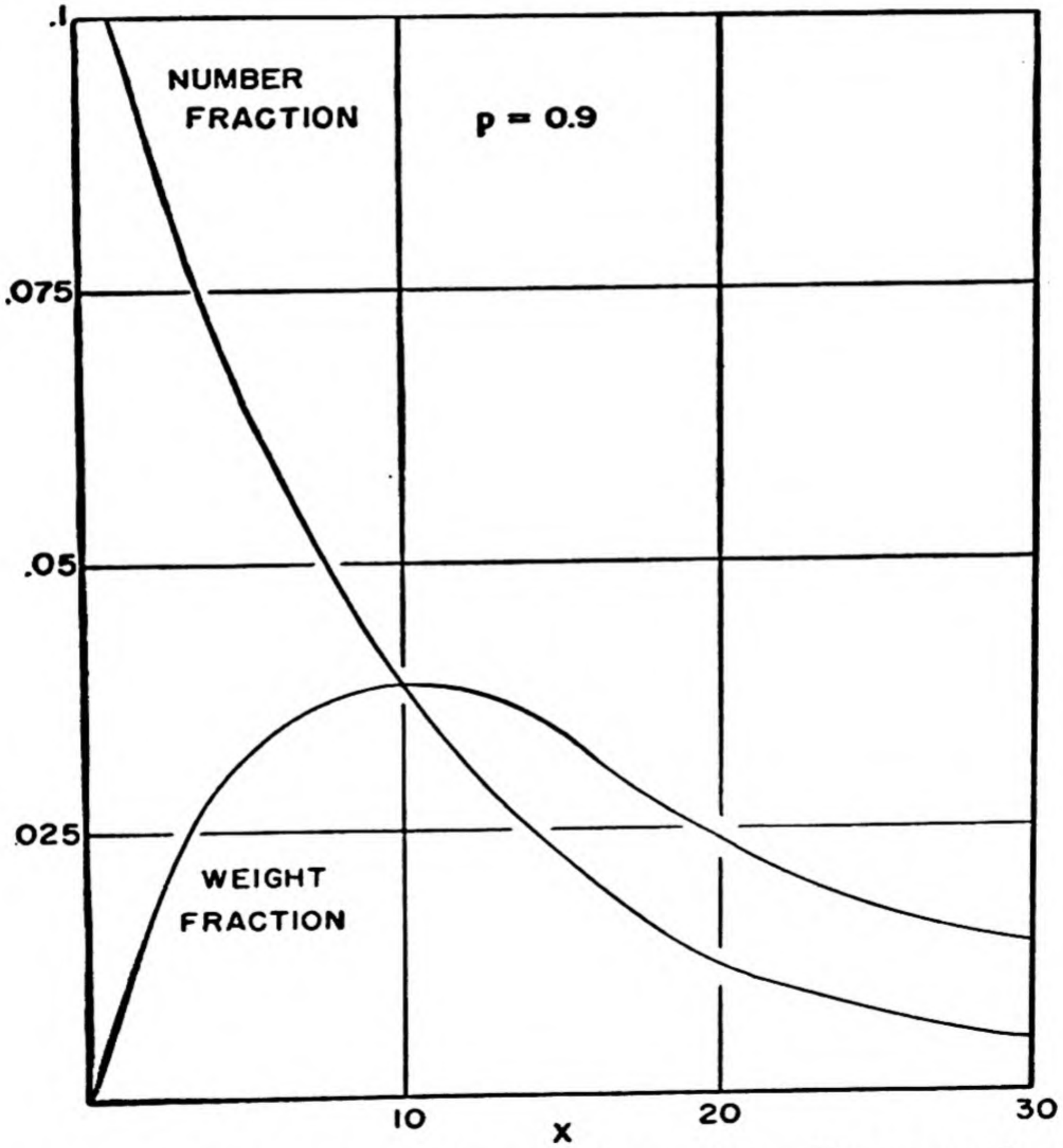



**Fig. 3.1.** Weight and number fractions for a linear condensation polymer, whose degree of polymerization, $p$, is equal to 0.9, plotted as a function of the number of segments per molecule.

Figure 3.1 illustrates the variation of $N_x$ and $W_x$ with $x$ for a value of $p$ equal to 0.9. It is interesting to note that $N_x$ has no maximum but decreases continuously as $x$ increases; this means that the most probable distribution, which is assumed to be the equilibrium distribution, is such that monomers are always more abundant than dimers, dimers more abundant than trimers, etc. regardless of the extent of polymerization $p$. If the distribution is, for any particular reason, not the equilibrium distribution, then on melting the polymer or on long standing, internal rearrangements of the type

$$2H\{HN(CH_2)_y NHCO(CH_2)_z CO\}_2 OH \rightarrow H\{HN(CH_2)_y NHCO(CH_2)_z CO\} OH + H\{HN(CH_2)_y NHCO(CH_2)_z CO\}_3 OH$$

will occur, which eventually will re-establish the equilibrium distribution.

### 3-3. *Applications*

To find the value of $x$ that gives the maximum value of $W_x$, at constant $p$, Eq. (3.2.5) is differentiated with respect to $x$, and the differential is set equal to zero.[3] The result is

$$x = -\frac{1}{\ln p} \tag{3.3.1}$$

We can also find the value of $p$ to choose so that $W_x$ will have a maximum at any selected value of $x$ by differentiating (3.2.5) with respect to $p$ at constant $x$; we obtain

$$p = \frac{x - 1}{x + 1} \tag{3.3.2}$$

An interesting question concerning the linear condensation polymer has to do with the molecular weight to be assigned to the mixture of long chain molecules of many different lengths. We must take an average of the molecular weights of the different molecules, but the average will depend on the method of averaging. Two molecular weight averages are in common use, the so-called number average molecular weight $\bar{M}_n$ and the weight average molecular weight $\bar{M}_w$ defined by the equations

[3] Note that $\partial a^u/\partial x = a^u \ln a(\partial u/\partial x)$.

$$\bar{M}_n = \frac{\sum_{x=1}^{\infty} M_x N_x}{\sum_{x=1}^{\infty} N_x} \tag{3.3.3}$$

and

$$\bar{M}_w = \frac{\sum_{x=1}^{\infty} M_x w_x}{\sum_{x=1}^{\infty} w_x} \tag{3.3.4}$$

where $M_x$ is the molecular weight of a polymer molecule $x$ segments long, $N_x$ and $w_x$ are the moles and weights of the $x$-mer.

Letting $M_0$ be the average molecular weight of the segments of which the polymer is composed, then

$$M_x = xM_0$$

$$w_x = M_x N_x = xM_0 N_x$$

Hence

$$\bar{M}_n = \frac{M_0}{1-p} \tag{3.3.5}$$

The equation for $\bar{M}_w$ becomes on substituting for $w_x$,

$$\bar{M}_w = \frac{M_0^2 \, \Sigma \, x^2 N_x}{M_0 \, \Sigma \, x N_x}$$

or[4]

$$\bar{M}_w = M_0 \frac{1 + 4p + 9p^2 + \ldots}{1 + 2p + 3p^2 + \ldots}$$

$$\bar{M}_w = M_0 \frac{1+p}{1-p} \tag{3.3.6}$$

The ratio of $\bar{M}_w$ to $\bar{M}_n$ is

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + p$$

Hence if $p$ is close to unity, as it will be for large extents of polymerization, the weight average molecular weight will be practically twice the number average molecular weight.[5]

[4] Note that $1 + 4p + 9p^2 + \ldots = (1+p)/(1-p)^3$.

[5] G. B. Taylor, *J. Am. Chem. Soc.*, **69**, 638 (1947) has experimentally verified the predictions of these statistical equations in the case of polyhexamethyleneadipamide (6-6 nylon).

There are many other applications of statistical methods to high polymers, which are interesting and important, but it is necessary to return now to the development of statistical thermodynamics before considering any other examples of the application of probability considerations.

## PROBLEMS

**1.** Calculate the degree of polymerization required to make the weight fraction of a decamer ($x = 10$) greater than the weight fraction of any other component of the polymer.

**2.** Calculate the degree of polymerization required to make the weight fraction of a decamer the greatest possible value during the polymerization.

**3.** Calculate the degree of polymerization required to make the number fraction of a decamer the greatest possible value during the polymerization.

**4.** Prove that no maximum exists in the plot of $N_x$ as a function of $x$.

**5.** Suppose that as an organic chemist you invent a new fiber and that the president of the corporation for which you work asks you to invent a new four-letter word for the fiber. How many possible words of four letters can be constructed out of our alphabet? (Do not bother to eliminate any four letter words now in use.)

## *Chapter 4*

# FUNDAMENTALS OF STATISTICAL MECHANICS: PROBABILITY EQUATION OF THE MOST PROBABLE STATE

4-1. Introduction. 4-2. Types and Magnitudes of Energies Possessed by Molecules. 4-3. The Population of Energy States. 4-4. The Probability of Different Distributions and the Conditions for the Maximum Probability. 4-5. The Probability of Fluctuations from the Distribution of the Most Probable State.

## 4-1. *Introduction*

The general methods of statistical mechanics on which statistical thermodynamics is based have been briefly reviewed in Chapter 1. It is not the purpose of this book to develop in detail the subject of statistical mechanics, which can be found elsewhere in a number of excellent treatises.[1] Instead, we shall give in this chapter a discussion of types of energy, and the population of energy states. Then will follow a simple derivation of the equations for the probability of the distribution of points in phase space, which in Chapter 5 will enable us to derive expressions for the population of energy states, or in other words, the Boltzmann equation. In this chapter we shall also investigate the probability of fluctuations from the most probable distribution.

[1] R. H. Fowler, *Statistical Mechanics*, 2d ed., Cambridge University Press, London, 1936; R. W. Gurney, *Introduction to Statistical Mechanics*, McGraw-Hill Book Co., Inc., New York, 1949; J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, Inc., New York, 1940; James Rice, *Introduction to Statistical Mechanics for Students of Physics and Physical Chemistry*, Constable & Co., London, 1930; G. S. Rushbrooke, *Introduction to Statistical Mechanics*, Oxford University Press, New York, 1949; R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, New York, 1938; R. C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, The Chemical Catalog Co., New York, 1927.

## 4-2. *Types and magnitudes of energies possessed by molecules*

When we say that an electron, atom, or molecule is in a certain energy state, we mean that the electron, atom, or molecule possesses that quantity of energy. It is quite possible that no atom, for example, will possess a particular selected amount of energy; in which case we speak of that energy state being empty. A hydrogen atom, for example, has one extranuclear electron; this electron can occupy a number of different energy levels in the hydrogen atom, or in other words, the hydrogen atom can possess a number of different energies. As the electron can be in only one energy state at a time, it is clear that there will be a number of vacant energy levels within the hydrogen atoms. When we speak of energy or of free energy, we always mean energy relative to some standard energy, because we have no way of measuring absolute energies or free energies any more than we have of measuring absolute heights.

Because of the wave nature of material particles and because every material particle has a wave associated with it whose wavelength depends on the energy of the particle, it turns out that not all wavelengths or energies of the particle occur, but only those whose wave function and energies satisfy the famous Schrödinger wave equation. This means that the possible energy values due to the mechanical motions of the atoms and electrons involved are limited in number and are given in the solution of the Schrödinger wave equation as applied to the different types of motions. This is even true of translational motion such as exhibited by a particle bouncing around in a box. Thus if the box is a cube having sides $l$ cm. in length, and if the walls are perfectly reflecting so that no energy on collision is transmitted from the particle to the wall, and if the particle moves perfectly freely, that is to say, if its potential energy (energy of position) remains constant, then the possible translational energy states of the particle as given by the solution of the Schrödinger wave equation are

$$\epsilon_{tr} = \frac{h^2}{8ml^2}(k_x^2 + k_y^2 + k_z^2) \tag{4.2.1}$$

In Eq. (4.2.1), $h$ is Planck's constant, $m$ is the mass of the molecule, and $k_x$, $k_y$, and $k_z$ are the so-called quantum numbers associated with the components of the momentum of the particle along the $x$, $y$,

and $z$ coordinates. The maximum values of the $k$'s are limited by the total energy of the system.

According to the classical kinetic theory of gases the translational energy of a molecule can be expressed in terms of its components of momentum as follows:

$$\epsilon_{tr} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \qquad (4.2.2)$$

We also learn from the kinetic theory of gases that the average (we shall learn later just what kind of an average) kinetic energy of a gas particle is

$$\bar{\epsilon}_{tr} = \tfrac{3}{2}kT \qquad (4.2.3)$$

where $k$ is Boltzmann's constant and $T$ is the absolute temperature. At 300°K, the translational energy would be approximately 900 cal./mole or 0.039 electron volt per molecule. It is interesting to compare Eqs. (4.2.1) and (4.2.3); such a comparison is given as one of the problems at the end of the chapter.

Returning now to Eq. (4.2.1), it should be pointed out that the translational quantum numbers, $k_x$, $k_y$, and $k_z$ may be any positive integral numbers. Thus, the translational energy states available to any selected molecule for finite total energy are extremely numerous, but not infinite in number. These quantum numbers describe the quantum state, or energy state of the particle, in much the same way that a house number, with street, city, and state, describes the location of a dwelling. It may happen that different values of $k_x$, $k_y$, and $k_z$ lead to the same value of $\epsilon_{tr}$, for example, 6 different combinations of $k_x$, $k_y$, and $k_z$, such as 4, 5, 6 or 6, 5, 4, or 5, 6, 4, etc. can yield the same value of $\epsilon_{tr}$. We have then, six different quantum states of exactly the same translational energy for this particular case. This means that the state is sixfold degenerate, that the statistical weight of the state is equal to six, $g_{tr} = 6$.

It is not the purpose of this book to develop the subject of wave mechanics; nevertheless an elementary derivation of the Schrödinger wave equation is given in a later chapter.

In addition to translational energy, the molecule may also possess rotational energy, or energy due to rotation about an axis passing through the center of gravity of the molecule. According to classical theory (which for most molecules at most temperatures of interest

may be considered to be correct) the rotational energy is given by the equation

$$\epsilon_{rot.} = \tfrac{1}{2} \sum_i I_i \omega_i^2 \tag{4.2.4}$$

where $I_i$ is the moment of inertia about one axis, $\omega_i$ the angular velocity about that axis, and summation is taken over the number of axes needed to specify the [redacted] two in the case of rigid linear molecules that have [redacted], and three for all other molecules. [redacted] the molecules [redacted] the [redacted]. Monatomic molecules therefore possess no rotational energy. Later on in this book we shall define the moment of inertia and discuss methods of evaluating it from the known structure of molecules.

The kinetic theory of gases tells us that the average rotational energy of a rigid linear molecule, such as $O_2$ or $HC \equiv CH$, with two degrees of rotational freedom is

$$\bar{\epsilon}_{rot.} = kT \tag{4.2.5}$$

while nonlinear molecules with three degrees of rotational freedom (rotational motion expressible in terms of rotation about three selected axes) have the average rotational energy

$$\bar{\epsilon}_{rot.} = \tfrac{3}{2}kT \tag{4.2.6}$$

Thus the rotational energy is equal to the translational energy in this last case and equal to two-thirds of the translational energy in the case of the rigid linear molecules.[2]

Analogously to translational quantum states, the exact quantum rotational states of the molecule can be recovered only through solution of the Schrödinger wave equation as applied to the rotational motion; the result is, for the case of a rotating dumbbell (rigid linear molecule),

$$\epsilon_{rot.} = j(j+1)\frac{h^2}{8\pi^2 I} \tag{4.2.7}$$

[2] It is unnecessary to prove the validity of Eqs. (4.2.3), (4.2.5), and (4.2.6) from kinetic theory; this will be done by means of the statistical mechanical approach later on in this book.

where $j$ is the rotational quantum number having any positive integral value from zero to infinity. All rotational energy levels are degenerate except the ground level where $j$ is equal to zero (no rotational energy); the degeneracy or the statistical weight of each rotational energy level is given by the expression

$$g_{rot.} = 2j + 1 \tag{4.2.8}$$

Equation (4.2.8) follows from the quantum theory restriction that the projection of the angular momentum vector $(h/2)m$ along a selected fixed axis can have only certain values given by integral positive and negative values of $m$ from zero to $j$, or $2j + 1$ such values for $m$. In classical quantum theory, the different integral values of $m$ represent the different possible planes of motion.

The quantity

$$\frac{h^2}{8\pi^2 Ik} \tag{4.2.9}$$

has the dimensions of temperature; comparison of this "rotational temperature" for various molecules with customary temperatures is given as a numerical problem at the end of the chapter.

We shall consider later the rotational energy equation for nonlinear or flexible linear molecules.

Turning now to vibrational energy, it is obvious that a monatomic molecule cannot vibrate, consequently, it possesses no vibrational energy. All other molecules do, however, at all temperatures including absolute zero. The energies involved in vibration for a linear harmonic oscillator again may be obtained through the solution of the Schrödinger wave equation; the quantum states have the energies

$$\epsilon_{vib.} = (v + \tfrac{1}{2})hv_i \tag{4.2.10}$$

where $v$ is the vibrational quantum number whose integral values run from zero to infinity, and $v_i$ is the fundamental frequency of vibration for one vibrational degree of freedom. Actually, the total degrees of vibrational freedom are equal to the total number of degrees of freedom for the molecule, which is three times the number of atoms in the molecule, less the degrees of rotational and translational freedom. Thus benzene will have 36 − 6 or 30 vibrational degrees of freedom. Although each vibrational energy state by (4.2.10) is nondegenerate, statistical weight equal to unity,

actually vibrational energy levels can be degenerate by virtue of the fact that some of the modes of vibrational motion may have identical vibrational frequencies. Thus, in the complicated case of benzene, it is estimated that only 20 different fundamental modes of vibration exist, 10 doubly degenerate and 10 nondegenerate. To obtain the vibrational energy for the whole molecule it is necessary to sum (4.2.10) over all modes of vibration including all degenerate modes.

We shall not give the equation for the classical theory vibrational energies inasmuch as such high temperatures are required to attain the classical vibrational energies that the molecules usually decompose thermally before such temperatures are reached.

As a matter of fact, we have expressed the energies of the rotational and vibrational quantum states in the simplest possible equations; for high vibrational and rotational energies and for internal rotations complications ensue, which will be considered later.

The magnitude of vibrational energies may be very small or so large that the energy is without significance for thermodynamics at room temperature. The "vibrational temperature" is $h\nu/k$.

For most molecules, at least the simple ones, the difference of energy between the lowest electronic state of the molecules and the next higher state is so great that at all practical temperatures all molecules remain in their lowest electronic states. For example, in the case of molecular hydrogen the difference in energy between these two states is 11.2 electron volts, equivalent to 263 kg. cal. per mole. At room temperature $kT$ is equivalent to 0.026 electron volt. For oxygen the energy difference between the lowest and next higher electronic state is less, about 0.98 electron volt or 23 kg. cal. per mole. This corresponds to a kinetic theory temperature ($kT$) of about 11,000°C. By electron volts we shall always mean electron volts per molcule.

Nuclear energies are so very high, equivalent to kinetic theory temperatures of millions of degrees, that they will not concern us in this book.

The last and possibly the most important type of energy to be considered is the energy of chemical interactions, or chemical energy. Imagine two hydrogen atoms reacting at the absolute zero of temperature. Considerable energy will be released by this reaction, call it $\chi$, but the actually liberated energy will be reduced by the

vibrational energy retained by the molecule, $\frac{1}{2}h\nu$, which is called the zero point energy. Thus the chemical energy or energy of formation per molecule, $\epsilon_0$, is

$$\epsilon_0 = -(\chi - \tfrac{1}{2}h\nu)$$

This energy is calculated with reference to the energy of the separated atoms as zero, and is therefore always negative. It is the order of magnitude of the heat of formation, that is, from 1 to 5 electron volts per molecule, usually.

In summary, then, the energies that chiefly interest us are translational, rotational, vibrational, and chemical energies.

## 4-3. *The population of energy states*

In any given isolated system of molecules, the total energy will be constant with time. Furthermore, if equilibrium exists, the various types of energy such as translational, rotational, etc. will also be constant with time. Each molecule will possess a certain amount of energy, $\epsilon_s$; if we let $n_s$ be the number of molecules possessing this energy, the total energy $E$ is obviously given by the summation

$$E = \sum_s n_s\epsilon_s \tag{4.3.1}$$

where the summation is to be taken over all the different groups of molecules having the different energies. The equation that tells us the number of molecules in each energy group is the distribution function that we need for the development of statistical thermodynamics. It will turn out that if the energy states are equally spaced and have equal statistical weights, the energy is divided up among the molecules so that the number of molecules having small energies is always greater than the number having larger energies. This is because the number of ways in which the energy can be distributed to produce such a division of the energy is greater than the number of ways any other distribution can be achieved, and since the probability is proportional to the number of complexions, the distribution with the greatest number of complexions is the most probable.

We can demonstrate this pictorially using a method similar to that of Gurney.[3] Suppose we consider the ideal linear harmonic oscillator whose energy levels are equally spaced in accordance with the equation for vibrational energies, Eq. (4.2.10). Let us consider

[3] R. W. Gurney, *Introduction to Statistical Mechanics*, McGraw-Hill Book Co., Inc., New York, 1949, Chap. 1.

three molecules labeled $a$, $b$, and $c$ and let us assume that the total vibrational energy to be shared by all three is equal to $3h\nu$ (omitting the zero point energy over which we have no control). All possible distributions of the three molecules consistent with these conditions are shown in Fig. 4.1. The configuration in which every molecule has one unit of energy, Fig. 4.1 (a), can arise in only one way and, is therefore the least likely to occur. The distribution, Fig. 4.1 (b), where one molecule has 3 units and two molecules have none can be formed in three ways and is more probable, while the distribution

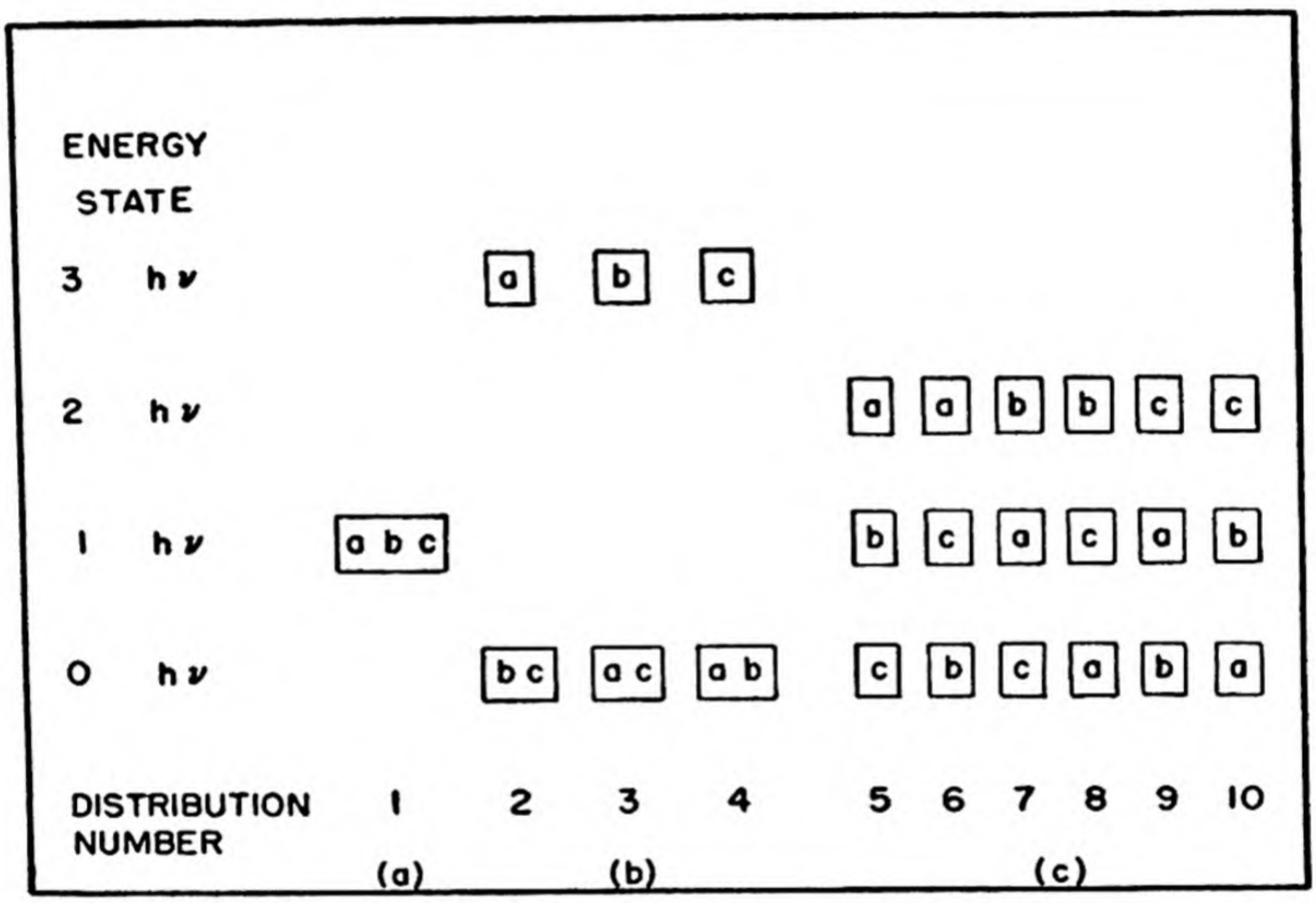



**Fig. 4.1.** Schematic distribution of molecules among four energy states.

in which one molecule has 2 units, one molecule has one unit and one molecule has none, Fig. 4.1 (c), can arise in six ways, and is therefore the most probable distribution of the group. Actually, we believe that in a collection of molecules, there is a continual interchange of energy between the molecules, so that molecule $a$ at one moment will have 3 units of energy, at the next moment it may have none, or two units, etc. We believe that as far as any one molecule is concerned, each quantum state is equally likely, with the reservation always in mind that the total energy must be constant; that is, all three molecules could not have 3 units of energy each at the same instant. In other words, the a priori probability and statistical weight of each quantum state of Fig. 4.1 are exactly the same as those of every other quantum state. In Fig. 4.1 there are ten different ways in

which the energy can be shared. We believe that each way is equally likely.

Now if we count the total number of molecules in each energy level for all possible configurations, we find 12 in the lowest or zero level, 9 in the next, 6 in the next, and only 3 in the highest. We see,

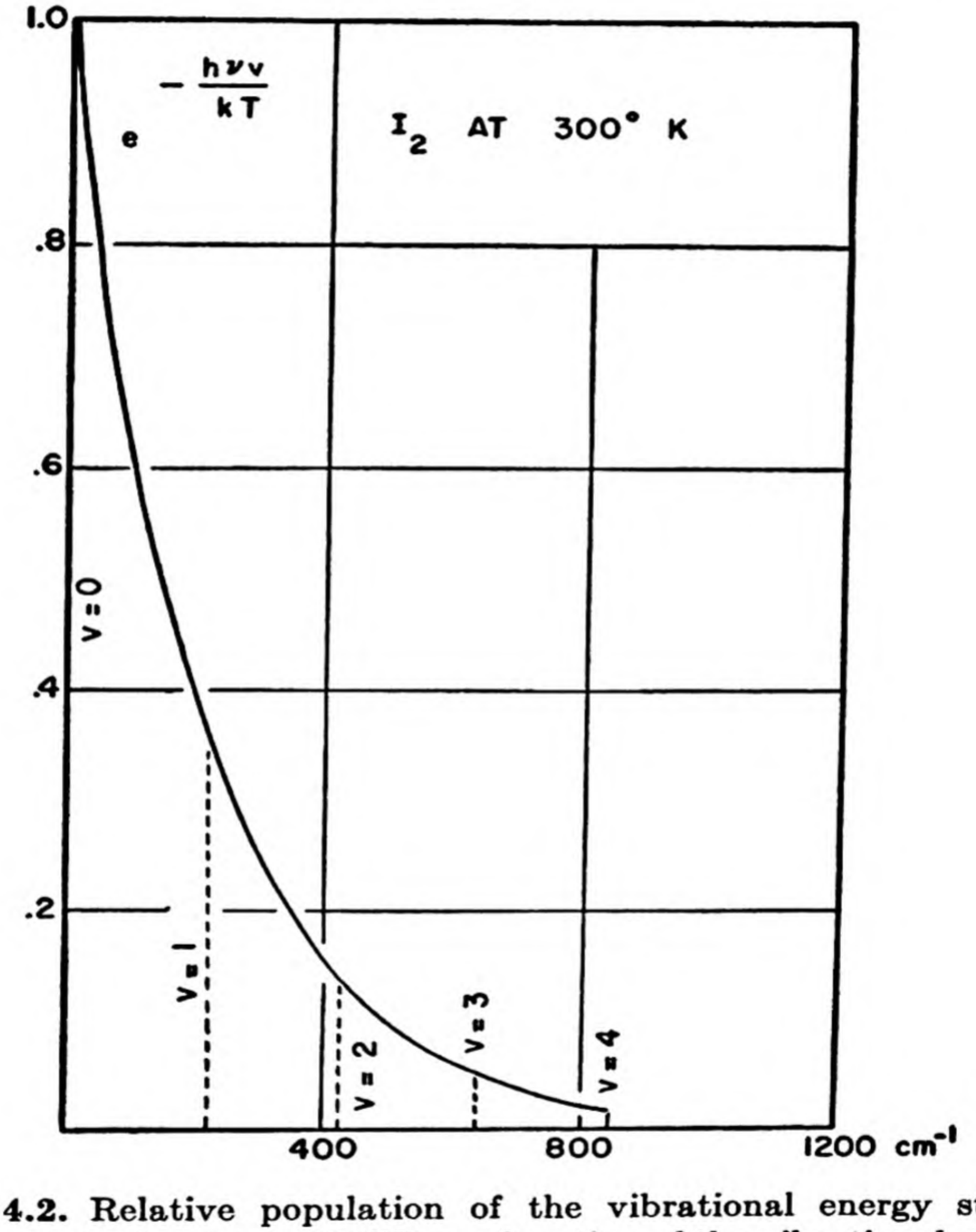



**Fig. 4.2.** Relative population of the vibrational energy states of iodine vapor molecules at 300°K as a function of the vibrational quantum number, $v$.

therefore, that the lowest level is the most populated and that the population of each level always declines as we go from a lower to a higher energy level. As will be proved later mathematically, this is a valid generalization for the vibrational energy states. Figure 4.2 illustrates the relative population of vibrational energy states for

the $I_2$ molecule at 300°K; and Fig. 4.3 the relative population of the rotational energy states for HCl at 300°K. The maximum in the latter curve results from the initial more rapid increase in the statistical weight of each level, $2j + 1$, than in the decrease of the Boltzmann factor.

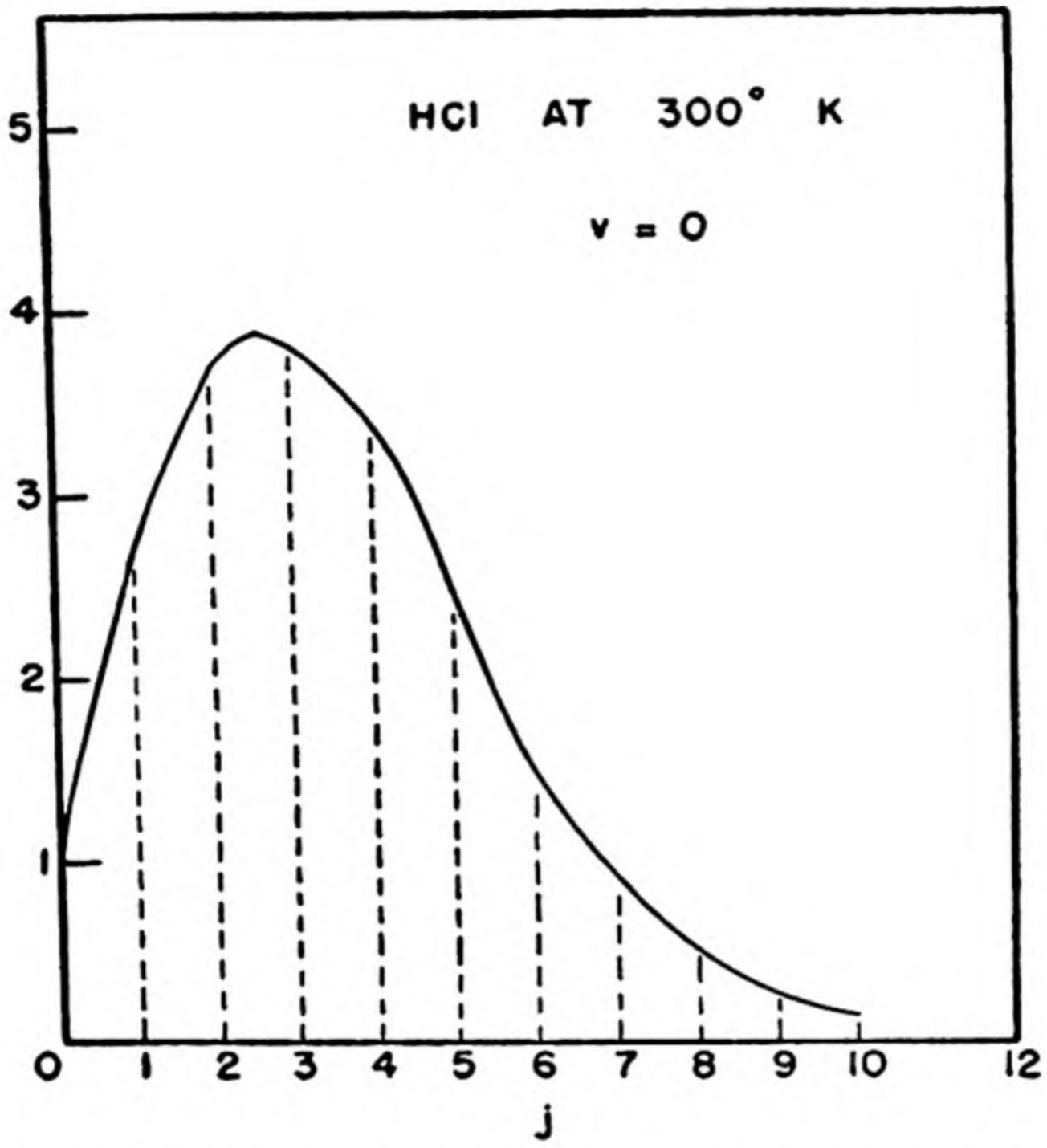



**Fig. 4.3.** Relative population of the rotational energy states of hydrogen chloride at 300°K in its ground electronic and vibrational state as a function of the rotational quantum number, $j$.

As Gurney points out, when the system under consideration contains many millions of molecules, the number of ways in which a "graded" configuration can be established becomes so overwhelmingly large in comparison with the number for unusual distributions such as indicated in Fig. 4.1 (a) that the latter can be completely neglected. A "graded" distribution is one in which the distribution of molecules in the different energy levels is such that the number of molecules continually diminishes with increase of energy content.

## 4-4. *The probability of different distributions and the conditions for the maximum probability*

When $n$ distinguishable molecules are distributed among $r$ energy states, the number of possible ways of doing this, not taking into

account the order [see Eq. (2.3.5)], so that there are $n_0$ molecules in the zero level, $n_1$ in the level number 1, etc., is given by the equation

$$C = \frac{n!}{n_0!n_1!n_2! \ldots n_r!} = \frac{n!}{\prod_{s=0}^{r} n_s!} \tag{4.4.1}$$

The total probability of such a distribution is equal to the number of ways such a distribution can be established as given by (4.4.1) multiplied by the compound probability of one such way, which is

$$\prod_{s=0}^{r} \omega_s{}^{n_s} \tag{4.4.2}$$

The total probability is therefore

$$W_{n_0,n_1,n_2\ldots} = n! \prod_{s=0}^{r} \frac{\omega_s{}^{n_s}}{n_s!} \tag{4.4.3}$$

Since the a priori probability is proportional to the statistical weight, let us write

$$\omega_s = \frac{g_s}{b}$$

and Eq. (4.4.3) as

$$W_{n_0,n_1,n_2\ldots} = \frac{n!}{(b)^n} \prod_{s=0}^{r} \frac{g_s{}^{n_s}}{n_s!} \tag{4.4.4}$$

Equation (4.4.4) is the probability of just one distribution; if we redistribute the molecules so that the numbers $n_0$, $n_1$, $n_2$, etc. change, we have a new distribution whose probability is also given by an equation such as (4.4.4). The sum of the probabilities of all possible distributions must equal unity; let this sum over all possible distributions be indicated by the symbol

$$\sum_{n_0 \ldots n_r} W_{n_0,n_1,n_2\ldots}$$

$$\sum_{n_0 \ldots n_r} W_{n_0,n_1,\ldots,n_r} = 1 = \frac{1}{(b)^n} n! \sum_{n_0 \ldots n_r} \prod_{s=0}^{r} \frac{g_s{}^{n_s}}{n_s!}$$

or

$$b^n = n! \sum_{n_0 \ldots n_r} \prod_{s=0}^{r} \frac{g_s{}^{n_s}}{n_s!} \tag{4.4.5}$$

Equation (4.4.4) can be written, therefore,

$$W_{n_0, n_1, n_2} = \frac{n! \prod_{s=0}^{r} \frac{g_s{}^{n_s}}{n_s!}}{n! \sum_{n_0 \ldots n_r} \prod_{s=0}^{r} \frac{g_s{}^{n_s}}{n_s!}} \tag{4.4.6}$$

Actually it is unnecessary to use $W$ in the form of (4.4.6); it is more convenient to use Eq. (4.4.4).

Let us now simplify Eq. (4.4.4) by taking logarithms of the equation, and applying the simplest form of the Stirling approximation, Eq. (2.5.4), to the logarithm of the factorials. We obtain

$$\ln W = n \ln n - n \ln b + \sum_{s=0}^{r} n_s \ln g_s - \sum_{s=0}^{r} n_s \ln n_s \tag{4.4.7}$$

In writing and simplifying (4.4.7) we have made use of the relation

$$n = \sum_{s=0}^{r} n_s$$

In order to find the most probable distribution or the values of $n_s$ corresponding to the most probable configuration, we allow $\ln W$ to undergo a small variation and set the variation equal to zero in order to obtain the conditions of maximum probability; thus

$$\delta \ln W = 0 = \sum_{s=0}^{r} \ln g_s \, \delta n_s - \sum_{s=0}^{r} \ln n_s \, \delta n_s \tag{4.4.8}$$

In obtaining (4.4.8) we have kept $n$ and $b$ constant during the variation and have also made use of the relation

$$\sum_{s=0}^{r} \delta n_s = 0$$

Rearranging (4.4.8) we obtain

$$\sum_{s=0}^{r} \ln \frac{n_s}{g_s} \, \delta n_s = 0 \tag{4.4.9}$$

as the condition to be satisfied in the case of the state of maximum probability. From this equation, the Boltzmann distribution law is

readily derived by the Lagrangian method of undetermined multipliers (see Chapter 5). At the moment, however, we wish to deduce from Eq. (4.4.9) a result of immediate interest, namely, the probability of a fluctuation from the most probable distribution (4.4.9).

## 4-5. *The probability of fluctuations from the distribution of the most probable state*

To calculate the probability of a state whose probability differs slightly from that of the most probable state, we calculate the ratio of $W + \delta W$ to $W$, where $\delta W$ represents a small change or increment in the probability. Returning to Eq. (4.4.7) we can write (remembering that $n$ and $b$ are constants) that

$$\ln (W + \delta W) = n \ln n - n \ln b + \sum_{s=0}^{r} (n_s + \delta n_s) \ln g_s - \sum_{s=0}^{r} (n_s + \delta n_s) \ln (n_s + \delta n_s) \qquad (4.5.1)$$

Subtracting (4.4.7) from (4.5.1) we find

$$\ln \frac{W + \delta W}{W} = \sum_{s=0}^{r} \delta n_s \ln g_s - \sum_{s=0}^{r} n_s \ln \frac{n_s + \delta n_s}{n_s} - \sum_{s=0}^{r} \delta n_s \ln (n_s + \delta n_s) \qquad (4.5.2)$$

Adding Eq. (4.4.9) to (4.5.2) and rearranging [the introduction of (4.4.9) now restricts $W$ to $W_{max.}$],

$$\ln \frac{W_{max.} + \delta W}{W_{max.}} = -\sum_{s=0}^{r} n_s \ln \left(1 + \frac{\delta n_s}{n_s}\right) - \sum_{s=0}^{r} \delta n_s \ln \left(1 + \frac{\delta n_s}{n_s}\right) \qquad (4.5.3)$$

The logarithm terms of (4.5.3) can be simplified and approximated by replacing them by a series expansion and dropping off all terms of the series beyond the first or first and second, provided that the variation in $n_s$, $\delta n_s$ is small in comparison with $n_s$. Thus, remembering that

$$\ln (1 + x) = x - \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 - \ldots$$

Eq. (4.5.3) can be reduced to

$$\ln \frac{W_{max.} + \delta W}{W_{max.}} = -\sum_{s=0}^{r} \delta n_s + \frac{1}{2} \sum_{s=0}^{r} \frac{(\delta n_s)^2}{n_s} - \sum_{s=0}^{r} \frac{(\delta n_s)^2}{n_s}$$

or

$$\ln \frac{W_{max.} + \delta W}{W_{max.}} = -\frac{1}{2} \sum_{s=0}^{r} \frac{(\delta n_s)^2}{n_s} \tag{4.5.4}$$

Equation (4.5.4) tells us that irrespective of the signs of the various fluctuations of the number of particles in all states $r$, the probability of the resulting distribution $W_{max.} + \delta W$ will be less than that of the probability of the distribution having the maximum probability, $W_{max.}$. Equation (4.5.4) also shows that as long as the square of the fluctuation, $\delta n_s$, is very small in comparison to $n_s$, the probability of the resulting distribution will not be greatly different from that of the maximum probability. In most physicochemical systems, $n_s$ will usually be large so that a considerable fluctuation $\delta n_s$ would have to occur to reduce the probability significantly. The probability also decreases exponentially with increase in the sum given by the right side of Eq. (4.5.4). As an illustration of (4.5.4) let us consider a distribution in which two compartments, each of unit volume, contain a perfect gas at standard conditions of temperature and pressure. Let us now imagine that the partition between the two compartments is removed and that a fluctuation in the number of molecules occurs such that 1% of the molecules in one compartment suddenly by random and kinetic motion diffuses into the other compartment. We ask ourselves what is the order of magnitude of the probability of the resulting distribution as compared with the equilibrium distribution. Here $r$ equals 2, $n_s$ is $3 \times 10^{19}$ molecules per cubic centimeter, and $\delta n_s/n_s$ is 0.01. Using these numbers we find that

$$\ln \frac{W_{max.} + \Delta W}{W_{max.}} = -3 \times 10^{15}$$

or

$$\frac{W_{max.} + \Delta W}{W_{max.}} = e^{-3 \times 10^{15}}$$

a number inconceivably small.

## PROBLEMS

**1.** Consider an $O^{16}O^{16}$ oxygen molecule whose mass is exactly 32 on the physicist's atomic weight scale. Imagine it to be contained in a 1 cm. cube at 300°K. What is its average kinetic energy in ergs as given by Eq. (4.2.3)? Assuming that the components of momentum in all three directions in space are equal, what must $p_x$, $p_y$, and $p_z$ be in order that the molecule shall possess the average translational energy? What must the translational quantum numbers also be to give this energy?

**2.** Compute the increase in temperature required to increase the translational energy to the same extent that an increase in $k_x$ by one unit would increase the translational energy in the range of values of $k_x$ calculated in problem 1. *Note:* Do not assume that the increase in temperature is negligible; derive an explicit expression for it and obtain the answer correct to 3 figures.

**3.** Repeat problems 1 and 2 for 10,000°K.

**4.** The moment of inertia of the oxygen molecule ($O^{16}O^{16}$) is $1.93 \times 10^{-39}$ g. cm.$^2$ Compute the increase in rotational energy in going from $j$ equal zero to $+1$. Compare this with the average kinetic energy.

**5.** Compute the value of $j$ necessary to yield a rotational energy for one oxygen molecule equal to its average rotational energy at 300°K as given by Eq. (4.2.5). *Note:* The answer will not be an integral number.

**6.** Suppose the $j$ value calculated in problem 5 to be increased by one unit; what would the corresponding increase in rotational energy be and what increase in temperature would this correspond to according to Eq. (4.2.5)?

**7.** Repeat problems 4, 5, and 6 for the case of the hydrogen molecule, $H^1H^1$, whose moment of inertia is $0.0466 \times 10^{-39}$ g. cm.$^2$

**8.** Calculate the rotational temperature for $H_2$, HD, $D_2$, and $O_2$ whose moments of inertia ($\times 10^{40}$) are 0.466, 0.621, 0.931, and 19.1 g. cm.$^2$, respectively.

**9.** Calculate the vibrational temperatures of $H_2^1$, $O_2^{16}$ and $K_2^{39}$, whose fundamental frequencies of vibration ($\omega_e$) are 4395, 1580, and 92.64 cm.$^{-1}$, respectively.

**10.** Calculate the number of ways in which 16 balls can be distributed into four compartments for the two following distributions:

(a) $n_1 = 2, \quad n_2 = 6, \quad n_3 = 6, \quad n_4 = 2.$
(b) $n_1 = 4, \quad n_2 = 4, \quad n_3 = 4, \quad n_4 = 4.$

**11.** If the a priori probability of each compartment is $\frac{1}{4}$ in problem 10, what is the probability of distributions (a) and (b)?

**12.** If the a priori probabilities of compartments 1, 2, 3, and 4 are $\frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{6}$, respectively, what are the probabilities of distributions (a) and (b)?

**13.** Consider the following two distributions of molecules among five (5) energy states:

| Distribution A | | Distribution B | |
|---|---|---|---|
| *Energy of state* | $n_s$ | *Energy of state* | $n_s$ |
| 0 | 17 | 0 | 16 |
| 1 | 8 | 1 | 8 |
| 2 | 2 | 2 | 4 |
| 3 | 2 | 3 | 2 |
| 4 | 2 | 4 | 1 |

(a) Calculate the total number of molecules.
(b) Calculate the total energy of each distribution.
(c) Calculate the number of ways each distribution can be established, assuming that the molecules are distinguishable.
(d) Which distribution is the more probable?

**14.** Change both the distributions A and B of problem 13 by adding one molecule to energy state 1 from each of the energy states 0 and 2, thus maintaining the total energy constant.
(a) Calculate again the number of ways each distribution can be established.
(b) Which distribution, that of problem 13 or 14 in each case (A and B), is the more probable?

**15.** Calculate the probability of a state in a colloidal system of 2 $cm.^3$ containing 5000 particles per cubic centimeter in which 10 particles have migrated spontaneously from one cubic centimeter to the other, relative to the probability of the state where each cubic centimeter contains 5000 particles.

# *Chapter 5*

# DERIVATION AND SIGNIFICANCE OF THE BOLTZMANN DISTRIBUTION LAW

5-1. Derivation of the Boltzmann Equation by the Method of Undetermined Multipliers. 5-2. Evaluation of the Constant $\alpha$. 5-3. The Partition Function. 5-4. Definition of Average Values in Statistical Thermodynamics. 5-5. The Average Energy and the Significance of the Constant $\beta$. 5-6. Quantum Derivation of the Boltzmann Equation. 5-7. The Maxweli Equation for the Distribution of Velocities and Other Forms of the Boltzmann Equation. 5-8. Average Velocities.

## 5-1. *Derivation of the Boltzmann equation by the method of undetermined multipliers*

Perhaps the most useful and, as a result, the most important equation in physical science is the Boltzmann distribution law. In fact, Schrödinger[1] has declared that the Boltzmann factor contains all of thermodynamics in a nutshell. It behooves us, therefore, to gain a thorough insight into the meaning and significance of this equation. Formally, it is most simply derived through use of a special mathematical method of solving equations for maxima or minima known as the Lagrangian method of undetermined multipliers.

We start with Eq. (4.4.9), which expresses the condition that must be satisfied for the state of maximum probability,

$$\sum_{s=0}^{r} \ln \frac{n_s}{g_s} \delta n_s = 0 \tag{4.4.9}$$

[1] E. Schrödinger, *Statistical Thermodynamics*, 2d ed., Cambridge University Press, London, 1952, p. 8.

However, for any physical system at equilibrium, the variables $n_s$ are not all independent, but must satisfy the conditions that the total number of molecules and the total energy remain constant, or

$$\sum_{s=0}^{r} \delta n_s = 0 \tag{5.1.1}$$

$$\sum_{s=0}^{r} \epsilon_s \, \delta n_s = 0 \tag{5.1.2}$$

To solve (4.4.9) under these conditions we multiply (5.1.1) by the undetermined multiplier $\alpha$, a constant independent of $\delta n_s$; hence

$$\sum_{s=0}^{r} \alpha \, \delta n_s = 0 \tag{5.1.3}$$

and (5.1.2) by the undetermined multiplier $\beta$, also independent of $\delta n_s$; hence

$$\sum_{s=0}^{r} \beta\epsilon_s \, \delta n_s = 0 \tag{5.1.4}$$

The constant $\beta$ has the dimensions of reciprocal energy in order that (5.1.4) will be a pure number.

As both (5.1.3) and (5.1.4) equal zero, we can add them to (4.4.9) without changing the value of (4.4.9) and obtain

$$\sum_{s=0}^{r} \left( \ln \frac{n_s}{g_s} + \alpha + \beta\epsilon_s \right) \delta n_s = 0 \tag{5.1.5}$$

Now, in the series represented by (5.1.5) the first two terms can be written

$$\ln \frac{n_0}{g_0} + \alpha + \beta\epsilon_0 = 0 \tag{5.1.6}$$

$$\ln \frac{n_1}{g_1} + \alpha + \beta\epsilon_1 = 0 \tag{5.1.7}$$

We can so choose $\alpha$ and $\beta$ that expressions (5.1.6) and (5.1.7) are individually equal to zero as written. If this is true, it is obvious that both $\delta n_0$ and $\delta n_1$ can be given any value whatsoever without invalidating (5.1.5). Now if $\delta n_0$ and $\delta n_1$ can be given any value, it follows that this is also true for all the other $\delta n_s$ values, because the

sum of all the $\delta n_s$ values must be equal to zero. By inspection of (5.1.5) it can be seen that the condition for maximum probability (5.1.5) can be satisfied if each of the quantities of the sum in the bracket is equal to zero. Because the quantities $\delta n_s$ can take on any value, subject to conditions (5.1.3) and (5.1.4), the only way in which (5.1.5) can be satisfied is for the separate terms in the brackets of (5.1.5) to be each equal to zero.

The two conditions that must be satisfied, (5.1.1) and (5.1.2), require the introduction of two undetermined multipliers.[2]

We can say, therefore, that in general

$$\ln \frac{n_s}{g_s} + \alpha + \beta\epsilon_s = 0$$

or

$$n_s = g_s e^{-\alpha} e^{-\beta\epsilon_s} \tag{5.1.8}$$

## 5-2. *Evaluation of the constant $\alpha$*

Since

$$\sum_{s=0}^{r} n_s = n$$

we have

$$n = e^{-\alpha} \sum_{s=0}^{r} g_s e^{-\beta\epsilon_s} \tag{5.2.1}$$

To simplify our equations, we write immediately

$$Q \equiv \sum_{s=0}^{r} g_s e^{-\beta\epsilon_s} \tag{5.2.2}$$

where $Q$ is the partition function, and we meet the mathematical definition of this important quantity for the first time. Equation (5.2.1) can now be written

$$e^{-\alpha} = \frac{n}{Q}$$

and the Boltzmann distribution law in the form

$$\frac{n_s}{n} = \frac{g_s e^{-\beta\epsilon_s}}{Q} \tag{5.2.3}$$

[2] The method of undetermined multipliers is described in a number of books such as in *Statistical Mechanics* by Mayer and Mayer, John Wiley & Sons, Inc., New York, 1940, p. 433; *Introduction to Statistical Mechanics*, by R. W. Gurney, McGraw-Hill Book Co., Inc., New York, 1949, p. 258; *Quantum Chemistry*, by K. S. Pitzer, Prentice-Hall, Inc., New York, 1953, p. 102.

For further discussion of the significance of $\alpha$, see Chapter 14. Before we evaluate the constant $\beta$, it is instructive to consider briefly the significance of the partition function.

## 5-3. *The partition function*

A thorough understanding of the partition function requires much further study and application, but a glimpse of its nature can be

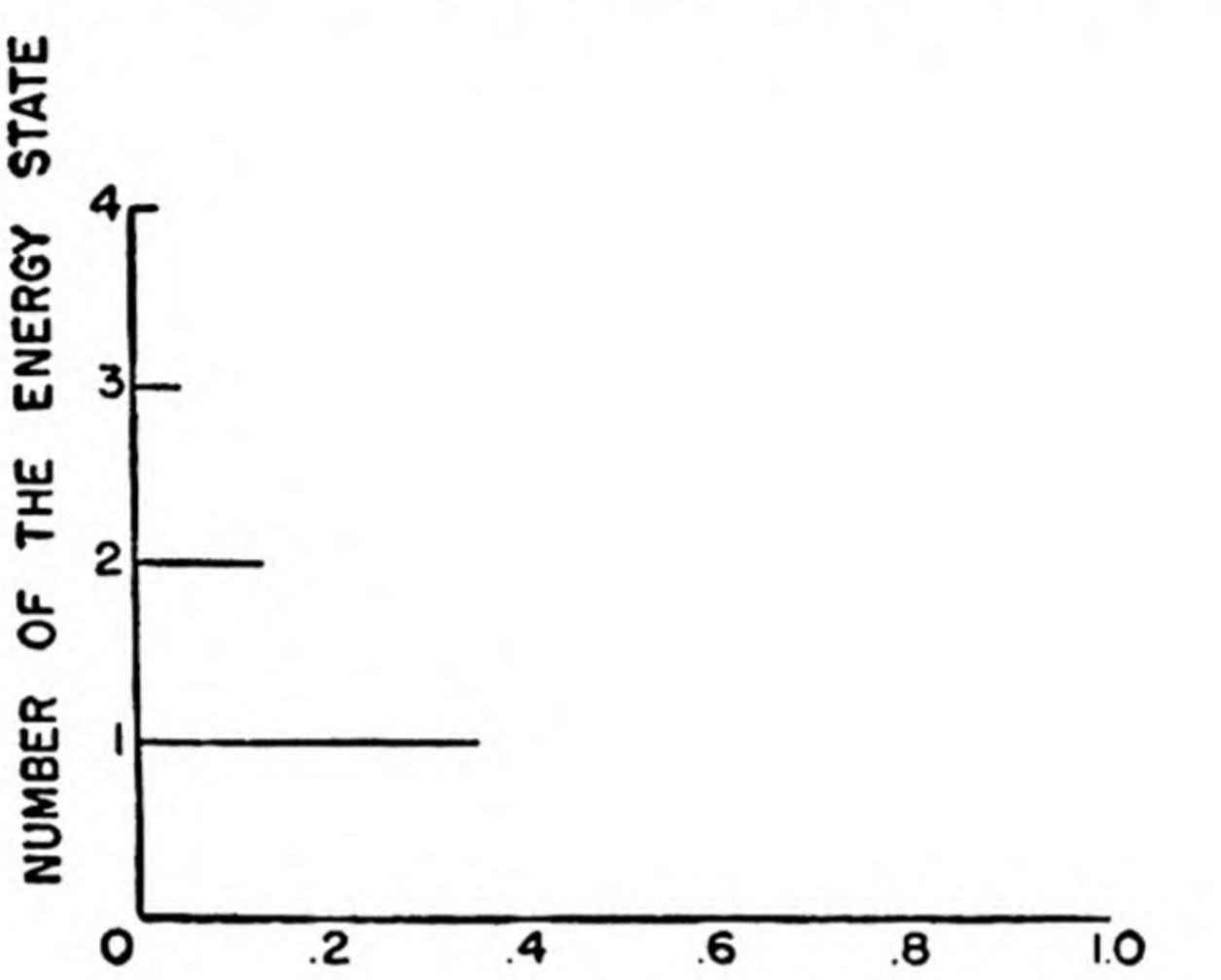



**Fig. 5.1.** Relative values of the Boltzmann factor for different energy states. The sum of the horizontal lines for all of the energy states, including the state of zero energy, is equal to the partition function.

obtained by expanding the summation (5.2.2) into a series of terms

$$Q = g_0 e^{-\beta\epsilon_0} + g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} + \ . \ . \ . \qquad (5.3.1)$$

Ordinarily, the energy of the lowest or ground state $\epsilon_0$ is taken to be zero, and if we assume that the statistical weights are all unity (no degenerate energy levels), the series (5.3.1) reduces to

$$Q = 1 + e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + \ . \ . \ . \qquad (5.3.2)$$

Now, the energy of state 2 is greater than that of state 1, of 3 greater than that of 2, etc., so that each term of (5.3.2) is smaller than the one immediately preceding it. Such a property can be graphically represented by Fig. 5.1, as Gurney[3] has done, where the length of

[3] R. W. Gurney, *Introduction to Statistical Mechanics*, McGraw-Hill Book Co., Inc., New York, 1949, p. 43.

each horizontal line represents the magnitude of a single term of the series. In fact, the lines of Fig. 5.1 are equal to the ordinates of the vibrational states of Fig. 4.2. The partition function, which always has the physical dimensions of a pure number, would be equal to the sum of the length of all the horizontal lines of Fig. 5.1. Figure 5.1 also illustrates the "graded" characteristic of the Boltzmann distribution law. The ordinates of Fig. 5.1 are the numbers of the energy states; if the energy states happen to be equally spaced, the ordinates could equally well represent the energy. The unit length of the lowest horizontal line results from the first term of the series when the energy of the lowest state is taken as zero.

## 5-4. *Definition of average values in statistical thermodynamics*

One of the useful applications of statistical thermodynamics is the definition and determination of average values of any function $F$. Such an average value is represented by the symbol $\bar{F}$ and is defined through the equation

$$\bar{F} = \frac{\sum_{s=0}^{r} F_s g_s e^{-\beta \epsilon_s}}{\sum_{s=0}^{r} g_s e^{-\beta \epsilon_s}} \tag{5.4.1}$$

where the denominator is the partition function. The definition of the average given by (5.4.1) is applicable to any quantity $F_s$ that is a function of the energy of the state $s$. That (5.5.1) is a logical definition of an average can be seen by considering the average energy. If $E$ is the total energy of the total number of molecules $n$, the average energy of each molecule $\bar{\epsilon}$ is given by the equation

$$\bar{\epsilon} = \frac{E}{n} = \frac{\sum_{s=0}^{r} \epsilon_s n_s}{\sum_{s=0}^{r} n_s} \tag{5.4.2}$$

But by the Boltzmann equation (5.2.3),

$$\sum_{s=0}^{r} n_s = \frac{n}{Q} \sum_{s=0}^{r} g_s e^{-\beta \epsilon_s} \tag{5.4.3}$$

and
$$\sum_{s=0}^{r} \epsilon_s n_s = \frac{n}{Q} \sum_{s=0}^{r} \epsilon_s g_s e^{-\beta \epsilon_s} \tag{5.4.4}$$

Dividing (5.4.4) by (5.4.3) in accordance with (5.4.2) we obtain

$$\bar{\epsilon} = \frac{\sum_{s=0}^{r} \epsilon_s g_s e^{-\beta \epsilon_s}}{\sum_{s=0}^{r} g_s e^{-\beta \epsilon_s}} \tag{5.4.5}$$

Comparison of (5.4.5) with (5.4.1) demonstrates the validity of the definition of average values (5.4.1). We shall now apply (5.4.1) to the determination of the average translational energy of gas molecules, from which in turn will come an insight into the significance of the undetermined multiplier $\beta$.

## 5-5. *The average translational energy and the significance of the constant* $\beta$

Consider a gas molecule such as a helium atom or a molecule of carbon dioxide. If the pressure of the gas is low, it can be considered that the gas behaves like a perfect gas; from the standpoint of energy considerations this is the same as saying that the energy of the molecule is not a function of position, that no potential energy due to interactions between molecules exists, that the energy, for example, of a monatomic molecule is all translational or kinetic (electronic and nuclear energy excepted). The velocity $v$ of a gas molecule can be expressed in terms of the components of the velocity $v_x$, $v_y$, $v_z$ along three axes in space such as the Cartesian coordinates $x$, $y$, $z$. The translational energy of one energy state for one molecule can be written

$$\epsilon_s = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2 \tag{5.5.1}$$

where $m$ is the mass of the molecule, or in terms of the components of the momenta,

$$\epsilon_s = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \tag{5.5.2}$$

Using (5.5.2) for the translational energy of state $s$, we can now write the statistical thermodynamic expression for the average of

the translational energy of a gas molecule, or

$$\bar{\epsilon} = \frac{\sum_{s=0}^{r} \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)}}{\sum_{s=0}^{r} e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)}} \tag{5.5.3}$$

Here the summation is to be taken over all values of the momenta; more exactly we should express the energy in terms of the wave mechanical energy states and sum over all values of the translational quantum numbers. But since it is sufficiently accurate to consider the translational energies from the classical standpoint, we can say that each component of the momentum can have all values from $-\infty$ to $+\infty$. We can also replace the summations of (5.5.3) by integrations over the momenta, since the energy levels are so closely spaced. Equation (5.5.3) now becomes

$$\bar{\epsilon} = \frac{1}{2m} \frac{\iiint_{-\infty}^{\infty} (p_x^2 + p_y^2 + p_z^2)e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)}\, dp_x\, dp_y\, dp_z}{\iiint_{-\infty}^{\infty} e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)}\, dp_x\, dp_y\, dp_z} \tag{5.5.4}$$

Because the components of the momenta are all independent of each other, the triple integrals of (5.5.4) are separable into individual and definite integrals[4] of the form

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2}\, dx = \frac{1}{2}\sqrt{\frac{\pi}{a^3}} \tag{5.5.5}$$

and

$$\int_{-\infty}^{\infty} e^{-ax^2}\, dx = \sqrt{\frac{\pi}{a}} \tag{5.5.6}$$

Performing the indicated integrations, we obtain the remarkably simple result

$$\bar{\epsilon} = \frac{3}{2} \cdot \frac{1}{\beta} \tag{5.5.7}$$

From the kinetic theory of gases it is known that the average translational energy of a gas molecule is $\frac{3}{2}kT$; hence it would appear that

$$\beta = \frac{1}{kT} \tag{5.5.8}$$

[4] See Table 7, Appendix, for some useful integrals.

Although we shall prove later by statistical thermodynamic methods that $\beta$ is proportional to the reciprocal of the absolute temperature, we shall adopt at once the value of $\beta$ given by (5.5.8) because there seems to be no point in keeping $\beta$ an unknown and mysterious quantity when its significance in terms of the average energy is so obvious.

## 5-6. *Quantum derivation of the Boltzmann equation*

At this point we digress slightly to give another derivation or deduction of the Boltzmann equation from which we obtain an added understanding of this important relation.[5] We call it a quantum derivation because it is obtained by considering the transfer of two particles from their quantum states to another intermediate state of such magnitude of energy that the total energy remains constant. Thus, if energy states 0, 1, and 2 are equally spaced, removing one molecule from state 0 and one from state 2 and adding both to state 1 causes no change in the total energy. Now if the distribution of particles among all the energy states is the most probable one, a change in the distribution due to the transfer of an infinitesimal number of particles such as 2 out of $10^{10}$ from one state to another would not change the probability. The probability of the first configuration can be expressed by the equation

$$W = \frac{n!}{n_0!n_1!n_2! \ \ldots} \cdot \frac{g_0{}^{n_0}g_1{}^{n_1}g_2{}^{n_2} \ \ldots}{b^n} \tag{5.6.1}$$

and the probability of the system after the transfer of two molecules by the equation

$$W' = \frac{n!}{(n_0-1)!(n_1+2)!(n_2-1)! \ \ldots} \cdot \frac{g_0{}^{n_0-1}g_1{}^{n_1+2}g_2{}^{n_2-1} \ \ldots}{b^n} \tag{5.6.2}$$

Taking the ratio of $W'$ to $W$ in order to find the ratio of probabilities, we obtain

$$\frac{W'}{W} = \frac{n_0 \cdot n_2}{(n_1+1)(n_1+2)} \cdot g_0{}^{-1}g_1{}^{2}g_2{}^{-1} \tag{5.6.3}$$

The statistical weights may be assumed to be equal to each other; then remembering that the number $n_1$ is much larger than 1 or 2 so

[5] This treatment is taken and modified from R. W. Gurney, *Introduction to Statistical Mechanics*, McGraw-Hill Book Co., Inc., New York, 1949, Chap. 1.

that the latter may be neglected in comparison to $n_1$, and that this infinitesimal transfer of particles does not change the probability, Eq. (5.6.3) reduces to

$$\frac{n_0}{n_1} = \frac{n_1}{n_2} \tag{5.6.4}$$

In fact, it can be shown in general that if the energy levels are equally spaced (5.6.4) becomes valid for any group of adjacent levels; in other words, the numbers $n_0$, $n_1$, $n_2$, $n_3$, etc. constitute a geometrical progression.

Let us now consider the case where the energy levels are not equally spaced; let us suppose, for example, that the difference in energy between the zeroth and the first level is equal to $a$ and between the first and second level equal to $b$. Suppose $p$ molecules are moved from the zeroth to the first level and $q$ molecules transferred from the second to the first level. In order that the total energy remain unchanged, it is necessary that

$$ap = bq \tag{5.6.5}$$

The ratio of the probability of the distribution after the transfer of $(p + q)$ molecules to that before the transfer is, analogously to (5.6.3),

$$\frac{W'}{W} = \frac{[(n_0)(n_0-1) \ . \ . \ . \ (n_0-p+1)][(n_2)(n_2-1) \ . \ . \ . \ (n_2-q+1)]}{(n_1+1)(n_1+2) \ . \ . \ . \ (n_1+p+q)} \tag{5.6.6}$$

or, since $n_0$, $n_1$, and $n_2$ are very large numbers, and since $W'$ equals $W$,

$$(n_1)^{p+q} = n_0{}^p \cdot n_2{}^q \tag{5.6.7}$$

Now let us assume that the distribution of molecules follows the exponential form

$$\begin{aligned} n_s &= Ae^{-\beta\epsilon_s} & n_1 &= Ae^{-\beta\epsilon_1} \\ n_0 &= Ae^{-\beta\epsilon_0} & n_2 &= Ae^{-\beta\epsilon_2} \end{aligned} \tag{5.6.8}$$

Substituting in (5.6.7) and remembering that

$$\epsilon_1 - \epsilon_0 = a \qquad \epsilon_2 - \epsilon_1 = b$$

we obtain

$$e^{q(\epsilon_2-\epsilon_1)} = e^{p(\epsilon_1-\epsilon_0)}$$

or

$$bq = ap$$

in agreement with (5.6.5).

This treatment demonstrates that the exponential or Boltzmann distribution satisfies the conditions of constant energy and constant total number of particles, and is consistent with the relation (5.6.7).

## 5-7. *The Maxwell equation for the distribution of velocities and other forms of the Boltzmann equation*

Instead of writing the Boltzmann equation in its most general form, (5.2.3), let us consider the ratio of the number of molecules in two energy states, say the first and the second. We obtain

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\beta(\epsilon_2 - \epsilon_1)} \tag{5.7.1}$$

Suppose we consider the number $n_+$ of positive ions per cubic centimeter, in a volume element $dV$ where the potential energy of the positive ion is $q_+\psi$ ($\psi$ is the electric potential in the volume element $dV$, and $q_+$ is the electric charge on the positive ion). If the average number of positive ions per cubic centimeter is $n$, and if we take the zero of energy as the potential energy of the ion where its concentration is equal to the average concentration, we obtain, on applying the Boltzmann distribution law,

$$n_+ \, dV = ne^{-\beta q_+ \psi} \, dV \tag{5.7.2}$$

and for the negative ions,

$$n_- \, dV = ne^{+\beta q_- \psi} \, dV \tag{5.7.3}$$

Equations (5.7.2) and (5.7.3) constitute the starting point in the Debye-Hückel theory of interionic attraction (Chapter 6).

Suppose we consider the number of polar molecules in the volume element $dV$ whose dipole axes make an angle $\theta$ with the direction of an electric field $F$. This number will be equal to the average number of molecules in the volume element at the angle $\theta$ in the absence of the field, $n$, multiplied by the Boltzmann factor, or

$$n_\theta \, dV = ne^{+\beta\mu F \cos\theta} \, dV \tag{5.7.4}$$

where $\mu$ is the dipole moment of the molecule and $-\mu F \cos\theta$ is the potential energy of the dipole in the electric field. Equation (5.7.4) is fundamental for the Debye treatment of polar molecules.

We now consider the Maxwell equation for the distribution of velocities among gas molecules. We begin by letting $n_s$, the number of molecules in the energy state $s$, be equal to $dn$, where $dn$ is the

number of molecules having velocities between $v$ and $v + dv$. Then $g_s$, the statistical weight of state $s$, will be taken as the six-dimensional volume element

$$dp_x\, dp_y\, dp_z\, dx\, dy\, dz$$

divided by $h^3$, where $h$ is Planck's constant, or

$$g_s = \frac{dp_x\, dp_y\, dp_z\, dx\, dy\, dz}{h^3} \tag{5.7.5}$$

The reasons for assigning this value to $g_s$ will be explained later; at the moment we can accept Eq. (5.7.5) without further discussion inasmuch as the exact value of the constant in the denominator of (5.7.5) is immaterial for derivation of the Maxwell equation. Suppose we let the $n$ of Eq. (5.2.3) be Avogadro's number $N$, and replace the summation of the partition function $Q$ by an integration of $dx\, dy\, dz$ over the volume of the container and of $dp_x\, dp_y\, dp_z$ over all values of the components of the momentum from minus infinity to plus infinity. We find that

$$\frac{dn}{N} = \frac{e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)}\, dp_x\, dp_y\, dp_z}{\int\int\int_{-\infty}^{\infty} e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)}\, dp_x\, dp_y\, dp_z} \tag{5.7.6}$$

inasmuch as

$$\int\int\int_0^{xyz} dx\, dy\, dz = V \tag{5.7.7}$$

(The values $dx$, $dy$, $dz$ are integrated to give the volume in both the numerator and denominator of (5.7.6)).[6]

Equation (5.7.6) was obtained by setting the energy of the molecule equal to the translational energy and assuming that the molecules have no potential energy, in other words that they move in field-free space (perfect gas). Performing the indicated integration in the denominator of (5.7.6), the equation reduces to

$$\frac{dn}{N} = \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)}\, dp_x\, dp_y\, dp_z \tag{5.7.8}$$

Suppose we consider a sphere of radius $p$.

$$p_x^2 + p_y^2 + p_z^2 = p^2 = m^2v^2$$

[6] Another way of considering Eq. (5.7.6) is to realize that we are interested only in the effect of the momenta on the distribution, because the distribution is independent of the values of $x$, $y$, $z$, since there is no potential energy. Consequently the fraction of molecules whose momenta lie in $dp_x$, $dp_y$, $dp_z$ depends only on a ratio of functions involving the momenta, not the volume.

and its differential volume $dV$ will be

$$dV = dp_x\, dp_y\, dp_z = 4\pi p^2\, dp = 4\pi m^3 v^2\, dv$$

Equation (5.7.8) can now be written in the form known as the Maxwell-Boltzmann distribution law:

$$\frac{dn}{N\, dv} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \tag{5.7.9}$$

where we have substituted $1/kT$ for $\beta$.

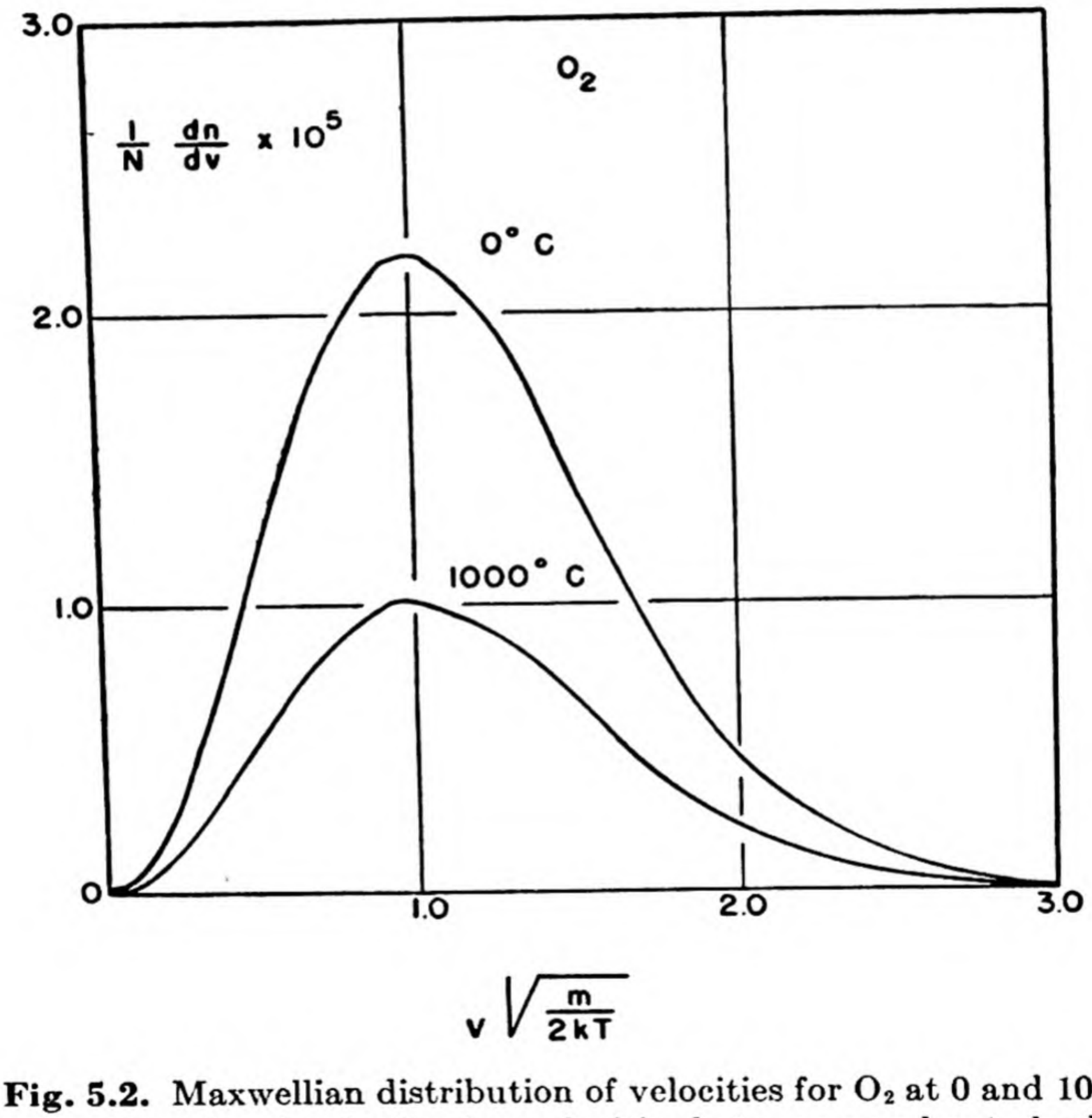



**Fig. 5.2.** Maxwellian distribution of velocities for $O_2$ at 0 and 1000°C. The fraction of molecules having velocities between $v$ and $v + dv$ plotted as a function of the dimensionless parameter, $v\sqrt{m/2kT}$.

In Fig. 5.2, $(dn/N\, dv)$ is plotted as a function of $v\sqrt{m/2kT}$. Inasmuch as (5.7.9) contains $v^2$, the value of $dn/N\, dv$ will be zero at zero velocity; furthermore, because of $v^2$ in the exponential, the function also becomes zero at infinite velocity. Accordingly, somewhere between zero and infinity for $v$, the function will pass through a

maximum, which can be shown to occur at a value of $v$ equal to $\sqrt{2kT/m}$.

The Maxwell distribution of velocities has been substantiated experimentally in a number of ways and as exactly as the difficulty of the experiment permits. We shall not describe these interesting experiments in this book.[7]

## 5-8. *Average velocities*

It is instructive to consider the methods of determining average velocities. We use our general definition of average values (5.4.1), replacing the summations by integrations because of the infinitesimal separation of translational energy states. Equation (5.4.1) can be used, of course, because the velocity is a function of the energy. Now there are several types of averages of the velocity to consider; we can determine the root mean square (r.m.s.) average, or the average of the absolute value of the velocity itself, or the velocity held by the largest number of molecules, which is the most probable velocity. We could also, if we wish, calculate the average $x$ component of the momentum or velocity, etc. As an example, let us calculate the root mean square average velocity. Applying Eq. (5.4.1) we obtain

$$\overline{v^2} = \frac{\sum_{s=0}^{r} v_s^2 g_s e^{-(\beta m v_s^2/2)}}{\sum_{s=0}^{r} g_s e^{-(\beta m v_s^2/2)}} \tag{5.8.1}$$

The bar over a symbol means the average value of that quantity. Replacing the summations by integrations and remembering that $dp_x\, dp_y\, dp_z$ is to be replaced by $4\pi m^3 v^2\, dv$, Eq. (5.8.1) reverts to

$$\overline{v^2} = \frac{\int_{-\infty}^{\infty} v^4 e^{-(\beta m v^2/2)}\, dv}{\int_{-\infty}^{\infty} v^2 e^{-(\beta m v^2/2)}\, dv} \tag{5.8.2}$$

After evaluating the integrals (see Appendix Table 7), we obtain

$$\overline{v^2} = \frac{3}{2}\left(\frac{2kT}{m}\right)$$

or

$$(\overline{v^2})^{1/2} = \sqrt{\frac{3kT}{m}} \tag{5.8.3}$$

[7] For a description of these experiments and references, see J. A. Eldridge, *Phys. Rev.*, **30,** 931 (1927); I. Estermann, O. C. Simpson, and O. Stern, *Phys-Rev.*, **71, 238** (1947).

which is the desired result. Note that (5.5.7) and (5.8.3) are in exact agreement with each other.

## PROBLEMS

**1.** Find the velocity that according to Maxwell's equation is held by the greatest number of molecules.

**2.** Derive the equation for the average positive $x$ component of the velocity of a molecule of a perfect gas.

**3.** Obtain the r.m.s. average for the $x$ component of the momentum of a molecule of a perfect gas.

**4.** Derive the equation for the average velocity of a molecule of a perfect gas. Repeat for the average speed.

**5.** Derive the equation for the density of gas at different levels above the earth's surface. (This is known as the hypsometric equation.) *Hint:* Let the potential energy $\phi$ of a molecule of mass $m$ at a height $h$ above the earth's surface be given by the equation

$$\phi = mgh$$

**6.** Derive the equation for the average height above ground for a gas molecule in the earth's gravitational field (at constant temperature).

**7.** Set up the expression for the average component of electric moment $\bar{m}$ in the direction of the electric field averaged over values of $\theta$ from zero to $\pi$.

# *Chapter 6*

# INTERIONIC ATTRACTION THEORY OF STRONG ELECTROLYTES

6-1. Statement and Thermodynamics of the Problem and Outline of the Theoretical Method to be Followed. 6-2. Mathematical Derivation of the Limiting Law. 6-3. The Equation for the Activity Coefficient and Test of the Theory. 6-4. Extensions of the Limiting Law. 6-5. Statistical Theory of Ion Association.

## 6-1. *Statement and thermodynamics of the problem and outline of the theoretical method to be followed*

Again we pause in our development of the principles of statistical thermodynamics for a chapter devoted to applications, this time to derivation of the fundamental limiting law of the Debye theory of interionic attractions for activity coefficients. As this chapter is not essential for those that follow, it may be omitted by the reader who is anxious to learn as rapidly as possible about the connection between thermodynamics and the Boltzmann distribution law.

Over the years 1890 to 1925 one of the most perplexing problems confronting physical chemists was that of interpreting the properties of solutions of highly conducting salts, acids, and bases. Many hypotheses were advanced, including several by a number of eminent scientists that were later proved to be essentially correct, but it was not until 1923, when Debye and Hückel,[1] then at the Technische Hochschule, Zürich, published their important contribution to solution theory, that a satisfactory basis was laid for a sound understanding of ionic solutions.

The partial molal free energy of an ion or the chemical potential $\mu_i$, of an ion in a solution is related to its mole fraction $N_i$ and its

[1] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923). See also *The Collected Papers of Peter J. W. Debye*, Interscience Publishers, Inc., New York, 1954.

activity coefficient $f_i$ by the equation[2] (which essentially defines the activity coefficient),

$$\mu_i = \mu_i + kT \ln N_i + kT \ln f_i \tag{6.1.1}$$

Now, if the solution were ideal, if the solute particles behaved ideally in the solution in the same way that gas molecules of a perfect gas behave ideally (no interaction between particles), the activity coefficient would be unity at all concentrations, and the chemical potential would follow the equation

$$\mu_{i\ (ideal)} = \mu_i^0 + kT \ln N_i \tag{6.1.2}$$

It was the thesis of Debye and Hückel that the entire difference in the chemical potential of an ion in a real solution as compared with an ideal solution, namely, the term $kT \ln f_i$, is due to the electric forces between ions and not to partial ionization, ionic hydration, or any of the other peculiarities postulated during the 1890–1925 era (such as ionic complex formation).

In developing their theory, Debye and Hückel made use of the Boltzmann equation to allow for the effect of temperature on the ionic distribution. They visualized a distribution of ions in the solution that would not be completely random as exists, let us say, for the molecules of sugar in a sugar solution. Although the ionic distribution is not completely random, on the other hand it is not completely ordered as in a crystal such as sodium chloride, because the thermal agitation of the solvent molecules imparts a kinetic motion to the ions that tends to break up their ordered array. The partly random, partly ordered distribution of ions is such, according to the postulates of Debye and Hückel, that in a small volume element of the solution in the neighborhood of a positive ion there will be on the time average a slightly greater concentration of negative ions than positive ions. It is easy to understand that a positive ion will attract electrostatically negative ions and repel other positive ions. Similarly, the concentration of positive ions in a small volume element near a negative ion will be slightly greater than the concentration of negative ions. This type of ionic distribution results

[2] In the excellent treatise *The Physical Chemistry of Electrolytic Solutions*, 2d ed., by H. S. Harned and B. B. Owen, Reinhold Publishing Corporation, New York, 1950, the reader will find a comprehensive treatment of the thermodynamics and interionic attraction theory of electrolytes.

in each ion having what Debye and Hückel call an "ionic atmosphere" surrounding it. The ionic atmosphere means simply the distribution of ions about a selected ion. Each ion is part of the ionic atmosphere of every other ion. For equilibrium in the solution the ionic atmosphere is spherically symmetrical about each ion, but when the ions move through the solution under the force of an applied electric field, or when one layer of solution moves over another as in viscous flow, the symmetrical arrangement of ions is disturbed and the ionic atmosphere is distorted. We shall not consider nonequilibrium phenomena in this book. Figure 6.1 illustrates the spherically symmetrical ionic distribution about a positive ion; at any distance $r$ from the ion, the electric potential $\psi$ is the same in all directions.

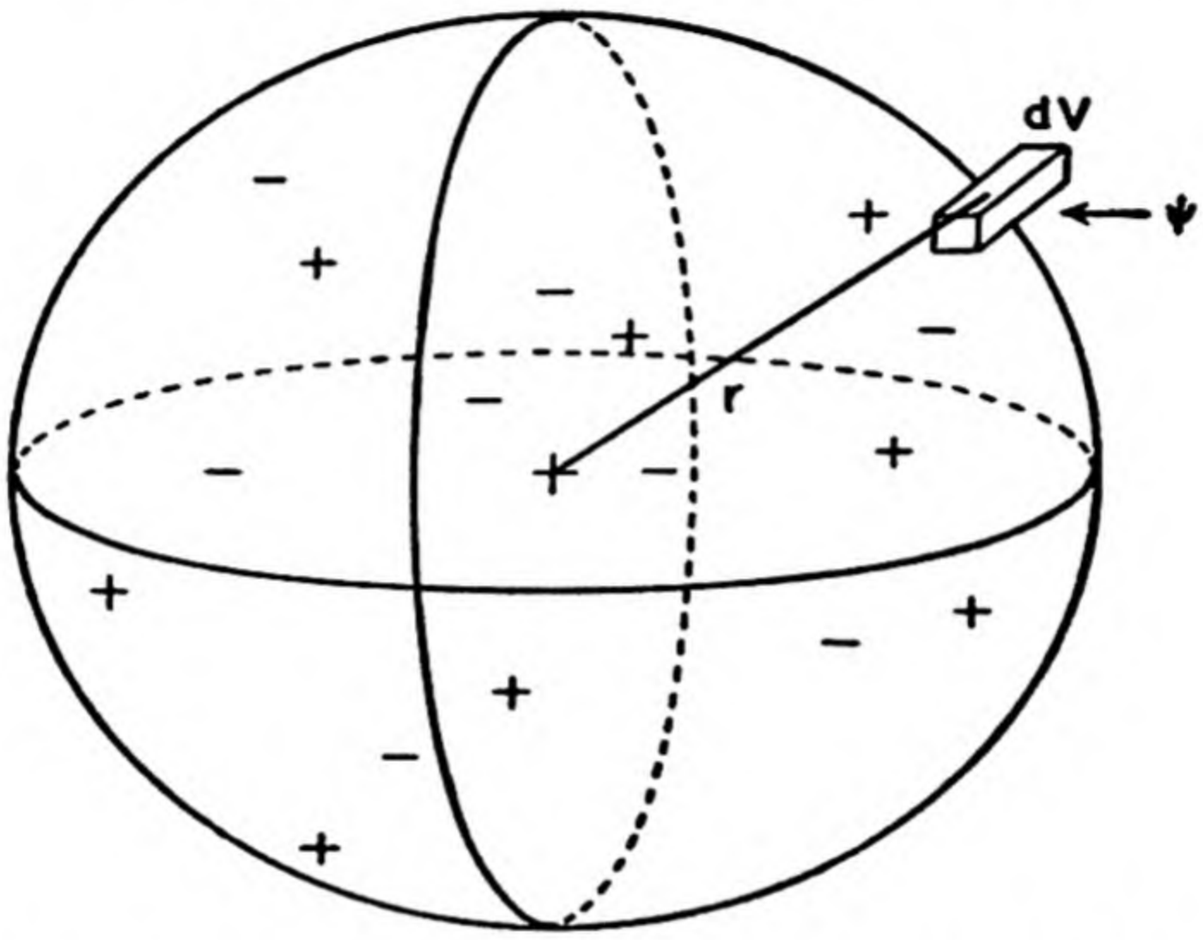



**Fig. 6.1.** Spherical section of electrolyte showing (1) a central positive ion with part of its ionic atmosphere, (2) an infinitesimal volume element, $dV$, at a distance $r$ from the central ion, in which an electric potential $\psi$ exists.

The sphere is to be thought of as filled with ions, with the electric potential $\psi$ the same everywhere over the surface of the sphere. Then $dV$ represents a small differential element of volume in the neighborhood of the positive ion. If we take an average of the number of positive and negative ions in $dV$ over a period of time, the negative ions will be found to predominate because of the proximity of the positive ion.

Debye and Hückel made use of the Boltzmann distribution law in the form of Eq. (5.7.2) to calculate the excess (negative excess)

concentration of positive ions over that of negative ions in the volume element $dV$. They then made use of a fundamental equation of electrostatics known as Poisson's equation, which is based on Coulomb's law

$$f = \frac{q_+ q_-}{Dr^2} \tag{6.1.3}$$

where $f$ is the force between two charged particles of charge $q_+$ and $q_-$, respectively, $r$ is the distance apart, and $D$ is the dielectric constant of the medium in which the charges are immersed (unity for a vacuum). Coulomb's law may also be expressed in the form

$$\psi_I = \frac{q_i}{rD} \tag{6.1.4}$$

This equation means that as the distance $r$ increases from a charge $q_i$ in a medium of dielectric constant $D$, the electric potential $\psi_I$ due to that charge decreases in accordance with (6.1.4). Equation (6.1.4) also tells us that the potential is directly proportional to the charge and inversely proportional to the dielectric constant of the medium. Since the Poisson equation relates the electric density $\rho$ at any point within the solution to the potential $\psi$ that exists at that same point, and since the Boltzmann distribution law leads to another equation also relating these two quantities, the problem is solved, at least in principle.

Knowing $\psi$, the electric potential at any point within the solution at a distance $r$ from the selected ion, Debye and Hückel showed how $\psi$ can be separated into the potential due to the centrally selected positive ion, and that due to all the other ions in the solution, or in other words, to the ionic atmosphere of the positive ion. It is the latter that is of importance, especially when calculated at the location of the positive ion, because to remove the positive ion from solution work has to be done against the attractive forces of the ions of the ionic atmosphere, and this work can be calculated in terms of the potential due to the ionic atmosphere. This electrical contribution to the free energy of the ion in solution can then be related to the term $kT \ln f_i$ of Eq. (6.1.1), and the problem is solved. In the course of the mathematical development, various simplifying mathematical approximations have to be made, which are strictly valid only at extreme dilutions. For this reason the Debye-Hückel

equation for the activity coefficient is called the "limiting law," which means that it is the expression to which the data become more and more into conformity as the concentration is lowered.

## 6-2. *Mathematical derivation of the limiting law*

We wish first of all to find the electric density $\rho$ in the volume element $dV$, at a distance $r$ from the selected positive ion. Electric density is defined as the excess positive or negative electric charge in $dV$ divided by the volume. We now make use of the Boltzmann distribution law, Eq. (5.7.2), to calculate the number of positive ions in $dV$; it is

$$n_+ \, dV = ne^{-q_+\psi/RT} \, dV \tag{6.2.1}$$

where $n$ is the stoichiometric number of positive ions per cubic centimeter. Equation (6.2.1) tells us that the more nearly the exponent $q\psi/kT$ approaches zero, the more nearly will the concentration of positive ions in $dV$ approach the average concentration of positive ions in the solution. High temperature, low concentrations (i.e., low $\psi$), or small charges on the ions all tend to reduce $q\psi/kT$ and so decrease the electrostatic influences. We can also see from Eq. (6.2.1) that $n_+$ will be greater than $n$ in the neighborhood of a negative ion ($\psi$ negative), and smaller than $n$ in the neighborhood of a positive ion ($\psi$ positive).

For simplicity, we shall develop the limiting law for salts composed of univalent ions; furthermore, except where indicated to the contrary, the valence $z_i$ of an ion will always be taken positive; i.e., the absolute value of $z_i$ will be used even for negative ions. The excess electric charge in $dV$ will be equal to

$$(n_+\epsilon - n_-\epsilon)dV \tag{6.2.2}$$

and the electric density

$$\rho = \frac{\epsilon(n_+ - n_-)dV}{dV}$$

or

$$\rho = \epsilon(n_+ - n_-) \tag{6.2.3}$$

Introducing the values of $n_+$ and $n_-$ given by the Boltzmann equation, we find that

$$\rho = n\epsilon(e^{-\epsilon\psi/RT} - e^{\epsilon\psi/RT}) \tag{6.2.4}$$

Equation (6.2.4) is too unwieldy to use as such, so Debye and Hückel introduced at this point perhaps the most serious approxima-

tion of the whole theory. They assumed that the electric energy $\epsilon\psi$ is much smaller than the thermal energy $kT$, so that the exponentials of (6.2.4) can be expressed by a series expansion in which only the first term in $\epsilon\psi/kT$ is retained. The electric energy $\epsilon\psi$ will be smallest for univalent ions at very low concentrations in media of high dielectric constant; hence under these conditions (6.2.4) may be replaced by an equation involving only the first terms in the series expansions. Remembering that

$$e^x = 1 + x + \frac{x^2}{2!} + \ldots$$

and that

$$e^{-x} = 1 - x + \frac{x^2}{2!} - + \ldots$$

we obtain

$$\rho = -2n\frac{\epsilon^2\psi}{kT} \tag{6.2.5}$$

as an approximate equation for the electric density.

The next step in the Debye-Hückel treatment is to combine Eq. (6.2.5), which relates the electric density to the potential, with the Poisson equation of electrostatics, which also relates the electric density to the potential. Thus with two equations and two unknowns $\rho$ and $\psi$, the problem is in principle solved. The Poisson equation states that at any point in a medium the divergence of the gradient, $\nabla^2$ (pronounced "del squared"), of the potential, or the second derivative of $\psi$ with respect to the three space coordinates

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

is equal to the negative of the charge density multiplied by $4\pi/D$, or

$$\nabla^2\psi = -\frac{4\pi\rho}{D} \tag{6.2.6}$$

Because it is rather difficult for students to acquire a mental picture of the significance of this equation, we shall try to illuminate it by the simplest possible derivation.[3] Consider a sphere of radius $a$ uniformly filled with electricity of density $\rho$, Fig. 6.2. According to Coulomb's law, the electric potential at the point $P$, which is $r$

[3] G. Jäger, *Theoretische Physik*, W. de Gruyter & Co., Berlin, 1922, Vol. 3, p. 12.

distant from the center, is given by the equation

$$\psi_P = \frac{2\pi\rho a^2}{D} - \frac{2}{3} \cdot \frac{\pi\rho r^2}{D} \tag{6.2.7}$$

Equation (6.2.7) is obtained by imagining the potential at $P$ to be the sum of two potentials $\psi_1$ and $\psi_2$; $\psi_1$ is the potential at $P$ due to all the electricity in the sphere for $r$ values smaller than $P$, and $\psi_2$ is the potential at $P$ due to the electricity within the sphere at all points outside the inner sphere of radius $r$, that is to say, within the

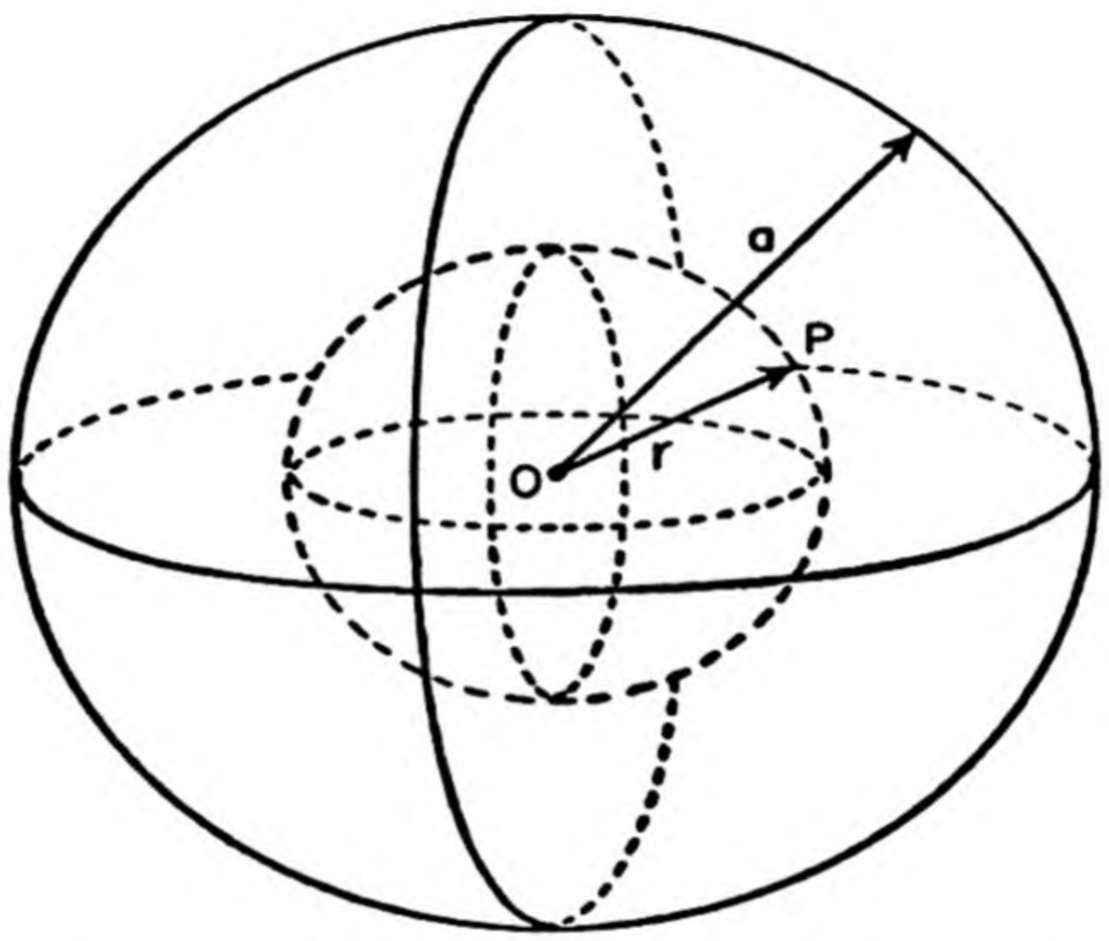



**Fig. 6.2.** Hypothetical sphere filled uniformly with electricity of density $\rho$, with an additional hypothetical inner sphere.

shell of inner radius $r$ and outer radius $a$. The first potential is equal to the total electric charge in the inner sphere divided by $Dr$, or

$$\psi_1 = \frac{q}{rD}$$

where

$$q = \frac{4}{3}\pi r^3 \rho$$

or

$$\psi_1 = \frac{4}{3} \cdot \frac{\pi r^2 \rho}{D} \tag{6.2.8}$$

The second contribution to the potential at $P$, $\psi_2$ is obtained by integrating from $r$ to $a$ the differential equation

$$d\psi_2 = \frac{4\rho\pi r^2\, dr}{Dr} \tag{6.2.9}$$

In (6.2.9), $\rho 4\pi r^2\, dr$ will be recognized as the total electric charge in a shell-shaped differential volume element of thickness $dr$. We find

$$\psi_2 = \frac{4\pi\rho}{2D}(a^2 - r^2) \tag{6.2.10}$$

which when combined with (6.2.8) yields (6.2.7). The Poisson equation is now readily obtained by performing on (6.2.7) the operation indicated by $\nabla^2$. This operator may be expressed in spherical polar coordinates by the sum of the terms

$$\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\,r^2\,\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2} \tag{6.2.11}$$

Because in an electrolyte unperturbed by any exterior forces, the ionic atmospheres of the ions are spherically symmetrical, the electric potential is independent of the angles $\theta$ and $\phi$, and the Poisson equation reduces to

$$\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\,r^2\,\frac{\partial\psi}{\partial r} = -\frac{4\pi\rho}{D} \tag{6.2.12}$$

Although this derivation of the Poisson equation was restricted to the case of a sphere uniformly filled with electricity, the Poisson equation[4] is in fact perfectly general and applicable to the problem of ionic solutions.

Returning now to the Debye-Hückel development, we can eliminate the electric density between Eqs. (6.2.5) and (6.2.12), obtaining as the fundamental differential equation of the Debye theory

$$\nabla^2\psi = \frac{8\pi\epsilon^2 n}{DkT}\,\psi \tag{6.2.13}$$

or

$$\nabla^2\psi = \kappa^2\psi$$

where

$$\kappa = \sqrt{\frac{8\pi^2\epsilon^2 n}{DkT}} \tag{6.2.14}$$

The quantity $\kappa$, which has the physical dimensions of reciprocal length, has a special significance in the Debye-Hückel theory as will be explained later. At this point it will be noted that $\kappa$ is proportional to the square root of the concentration inasmuch as $n$ is the number of ions per cubic centimeter. All the limiting laws for the properties

[4] A general derivation of the Poisson equation may be found in *Principles of Electricity*, by L. Page and N. I. Adams, Jr., D. Van Nostrand Company, Inc., New York, 1931, p. 83.

of ionic solutions, such as that for the logarithm of the activity coefficient, for the equivalent conductance, relative viscosity, and heats of dilution, contain the concentration to the one-half power, and it is this dependence of these properties on the square root of the concentration that was the first striking deduction of the Debye theory.

Equation (6.2.13) is a second-order differential equation, and has as a general solution the following equation for $\psi$:

$$\psi = A\frac{e^{-\kappa r}}{r} + A_1\frac{e^{\kappa r}}{r} \tag{6.2.15}$$

where $A$ and $A_1$ are constants of integration. The constant $A_1$ can immediately be set equal to zero, because it is a physical requirement that the electric potential $\psi$ approach zero as $r$ approaches infinity. This can be true only if $A_1$ is equal to zero, because the exponential term $e^{\kappa r}$ approaches infinity more rapidly than $r$ itself. The other constant of integration $A$ can be evaluated by determining the value of $\psi$ when $r$ approaches zero, where $\psi$ should approach the value of the potential, $\psi_I$ that the centrally selected ion would have if it were alone in the solution, namely,

$$\psi_I = \frac{\epsilon}{Dr} \tag{6.2.16}$$

To find the value of $\psi$ as $r$ approaches zero we expand the exponential term of (6.2.15) and then let $r$ approach zero. Thus,

$$\psi = \frac{A}{r}\left(1 - \kappa r + \frac{1}{2}\kappa^2 r^2 - + \ . \ . \ .\right) \cong \frac{\epsilon}{Dr} \tag{6.2.17}$$

We see from (6.2.17) that $A$ is equal to $\epsilon/D$. Rewriting (6.2.15) on inserting the values for $A$ and $A_1$, we obtain

$$\psi = \frac{\epsilon}{D}\cdot\frac{e^{-\kappa r}}{r} \tag{6.2.18}$$

as the potential in the ionic solution at a distance $r$ from an ion of charge $\epsilon$.

Now the potential $\psi$ includes the potential due to the charge on the ion itself, $\psi_I$ and that $\psi_{II}$ due to the charge of the ion's ionic atmosphere (the charge of the ionic atmosphere is always equal and opposite in sign to that of the selected ion). In order to compute the influence of the potential of the ionic atmosphere on the properties of the selected ion, we need to know $\psi_{II}$ exactly at the location of the selected ion [where the $r$ of Eq. (6.2.18) is equal to zero].

To find the value of $\psi_{II}$, we write

$$\psi = \psi_I + \psi_{II}$$

or since

$$\psi_I = \frac{\epsilon}{Dr}$$

then

$$\psi_{II} = \frac{\epsilon}{Dr}(e^{-\kappa r} - 1) \tag{6.2.19}$$

Inasmuch as $e^{-\kappa r}$ is less than unity, $\psi_{II}$ is opposite in sign and smaller than $\psi_I$. A typical set of values of $\psi$ and $\psi_{II}$ are plotted in Fig. 6.3 for

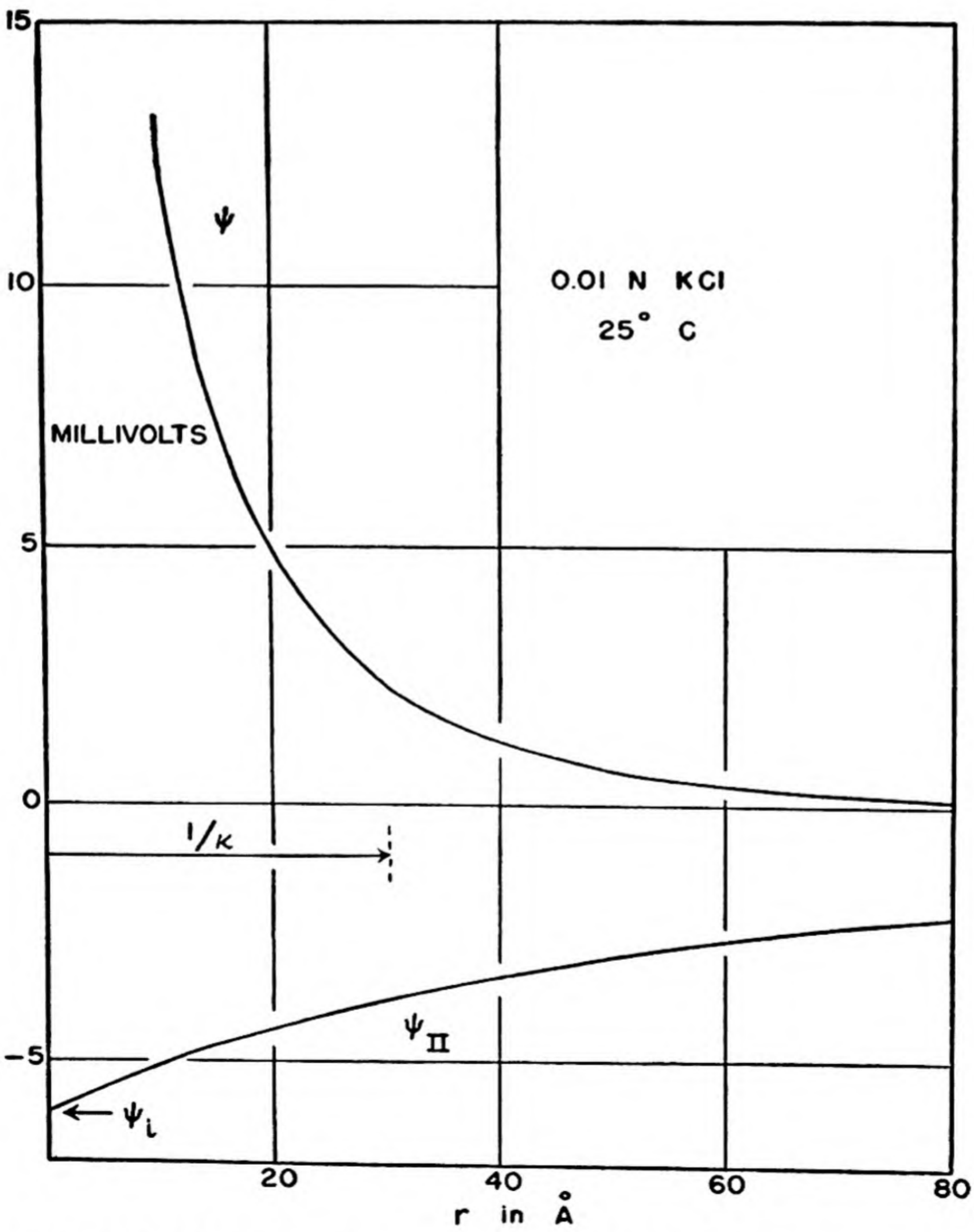



**Fig. 6.3.** Spherically symmetrical potential distribution about a centrally selected positive ion.

a uniunivalent electrolyte such as potassium chloride in water at 0.01 molar concentration at 25°C. Equation (6.2.19) gives the relation between $\psi_{II}$ and $r$, but we wish to know $\psi_{II}$ at $r$ equal to zero; in other words at the location of the selected ion itself. If we expand the exponential term of (6.2.19) in a series expansion, and let $r$

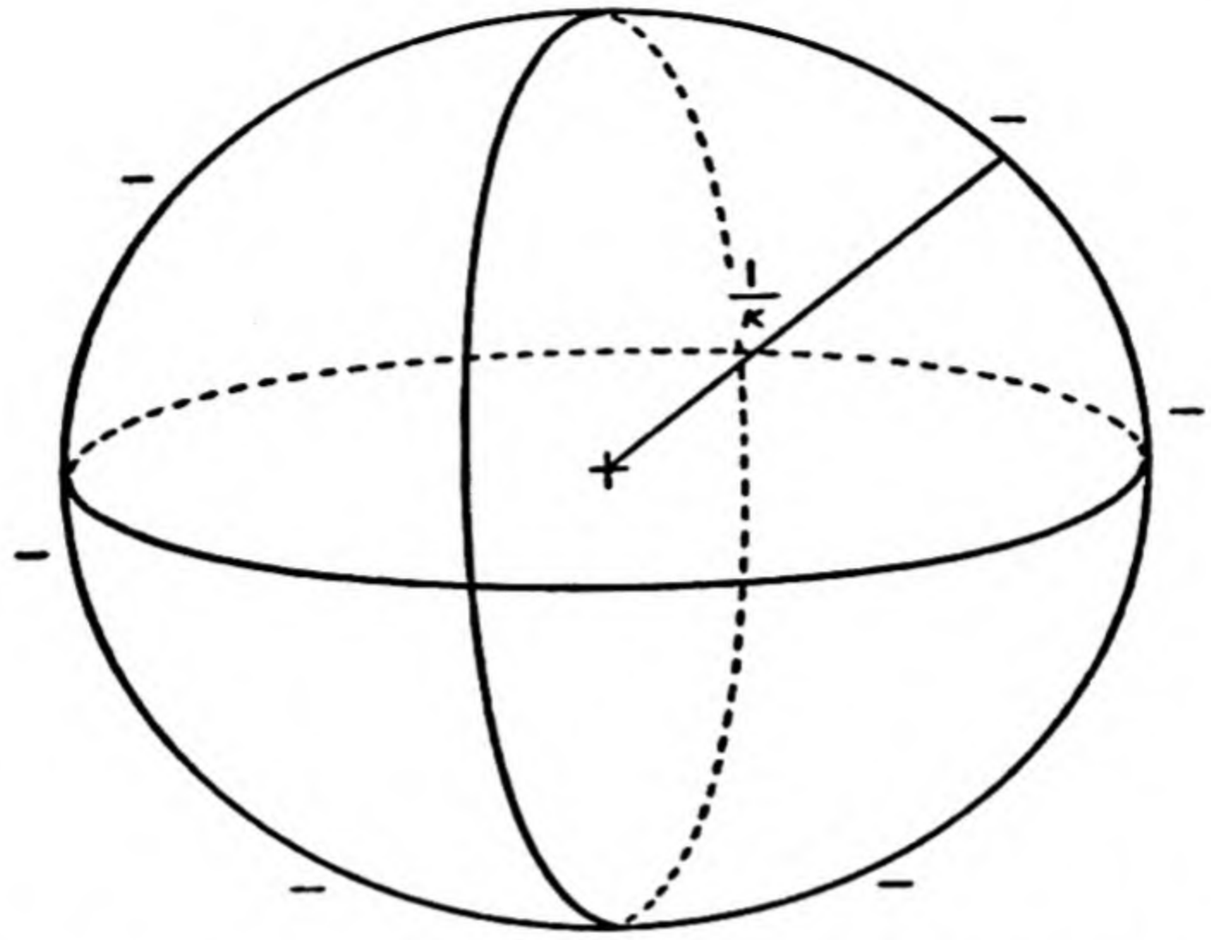



**Fig. 6.4.** Hypothetical spherical section of electrolyte to illustrate the significance of the distance $1/\kappa$. The total negative charge on the surface of the sphere should equal one unit.

approach zero, we obtain $\psi_i$, the potential due to an ion's ionic atmosphere at the location of the ion itself:

$$\psi_{II} = \frac{\epsilon}{Dr}(1 - \kappa r + \ldots - 1) \qquad (6.2.20)$$

hence

$$\psi_i = -\frac{\epsilon\kappa}{D}$$

The potential $\psi_i$ always has the sign opposite that of the charge on the selected ion. It is the value that the charge of the ionic atmosphere would produce on the selected ion if the charge of the ionic atmosphere were evenly distributed over the surface of a sphere surrounding the ion and having a radius equal to $1/\kappa$. Such a hypothetical situation is illustrated in Fig. 6.4.

The total potential is equal to $\psi_i/e$, and opposite in sign to $\psi_i$ at a value of $r$ equal to $1/\kappa$.

If we divide the solution surrounding the selected ion into concentric spherical shells of the same thickness $dr$, the net charge in

each shell has a maximum value when $r$ is equal to $1/\kappa$. As a consequence, we may consider the distance $1/\kappa$ to be a measure of the thickness of the ionic atmosphere; it is sometimes called the mean thickness of the ionic atmosphere. Since $\kappa$ is proportional to the square root of the concentration, we see why all the Debye limiting laws for the properties of strong electrolytes contain not the concentration directly, but the concentration raised to the 1/2 power.

At this point we should list various fundamental assumptions[5] of Debye and Hückel in addition to the neglect of higher terms in the expansion of (6.2.4). The validity of the Boltzmann distribution law as applied to ionic solutions is assumed; in other words, the Boltzmann distribution for the ions with their ionic atmospheres is assumed to be maintained. The theory requires that the mean distribution of charge in the neighborhood of a pair of ions $r$ distance apart is equal to the sum of the charges induced by the two ions separately (or that the potentials of the ionic atmospheres of two ions are additive). Physically, this requirement is undoubtedly met at high dilution for ions of small valence and large ionic diameters.

The treatment as given in this book assumes ions to be point charges; although it is not necessary to make this assumption, we shall not introduce ionic diameters into the Debye equation given here, but refer the reader to more extensive treatments[2] involving ionic diameters.

To calculate the influence of the interionic attractions on the activity coefficient of an ion by using equation (6.2.20), we may proceed in two ways: we may follow the original method of Debye and Hückel in which the total electric free energy of the solution is obtained and then differentiated with respect to the concentration to obtain the electrical contribution to the chemical potential of the ion, or we may calculate the latter directly according to the method of Guntelberg.[6] In the Debye method, in effect, all the ions of the solution are charged simultaneously in order to obtain the work of charging the ions. This work is the electrical contribution to the free energy or

$$F_{elec.} = n_0 \int_0^e \psi' \, dq \tag{6.2.21}$$

[5] The self-consistency and fundamental assumptions of Debye's theory are discussed by R. H. Fowler and E. A. Guggenheim, in *Statistical Thermodynamics*, University Press, Cambridge, 1939, pp. 383–394, 405–407.

[6] E. Guntelberg, *Z. physik. Chem.*, **123,** 199 (1926).

where $F_{elec.}$ is the electric (Helmholtz) free energy for $n_0$ ions of one kind, $q$ is the charge on the ion assumed to vary from zero to $\epsilon$ in the charging process, and

$$\psi' = -\frac{q\kappa'}{D} \tag{6.2.22}$$

In Eq. (6.2.22) both $q$ and $\kappa'$ vary during the charging process. Let

$$dq = \epsilon\, d\lambda$$

$$\kappa' = \frac{q}{\epsilon}\kappa = \lambda\kappa$$

$$\frac{q}{\epsilon} = \lambda$$

With these definitions, the equation for $F_{elec.}$ becomes

$$F_{elec.} = -\frac{n_0\kappa\epsilon^2}{D}\int_0^1 \lambda^2\, d\lambda = -\frac{1}{3}\cdot\frac{n_0\kappa\epsilon^2}{D}$$

or
$$F_{elec.} = -\frac{1}{3}\cdot\frac{{n_0}^{3/2}\epsilon^2}{D}\sqrt{\frac{8\pi\epsilon^2}{DkT}} \tag{6.2.23}$$

Differentiating (6.2.23) with respect to $n$ at constant $V$ and $T$ to obtain $\mu_{elec.}$, we find

$$\mu_{elec.} = -\frac{1}{2}\cdot\frac{\epsilon^2\kappa}{D} \tag{6.2.24}$$

In the Guntelberg charging process, the charge on the selected ion is built up from zero to $\epsilon$ with all the remaining ions in the solution already charged. Mathematically, this is equivalent to integrating (6.2.21) for one ion only, holding $\kappa$ constant, or

$$\mu_{elec.} = -\frac{\epsilon^2\kappa}{D}\int_0^1 \lambda\, d\lambda = -\frac{\epsilon^2\kappa}{2D}$$

as before.

Equating (6.2.24) to the nonideal term of the chemical potential, we have

$$kT \ln f_i = -\frac{\epsilon^2\kappa}{2D} \tag{6.2.25}$$

As already pointed out, it is the postulate of Debye and Hückel that in dilute solutions of strong electrolytes the term $kT \ln f_i$ in the

equation for the chemical potential arises entirely from the electric interactions between ions.

## 6-3. *The equation for the activity coefficient and test of the theory*

The mean ionic activity coefficient, $f_\pm$, is defined by the equation

$$f_\pm = (f_+^{\nu_+} f_-^{\nu_-})^{1/(\nu_+ + \nu_-)} \tag{6.3.1}$$

where $\nu_+$ is the number of positive ions one molecule dissociates into, and $\nu_-$ has the same meaning for negative ions, i.e., for $Al_2(SO_4)_3$,

$$\nu_{Al^{+++}} = 2; \qquad \nu_{SO_4^{--}} = 3$$

Rearranging (6.2.25) and solving for $f_\pm$, we obtain the important equation

$$\ln f_\pm = -z_+ z_- \frac{\epsilon^3}{(DkT)^{3/2}} \sqrt{\frac{\pi N}{1000}} \sqrt{\Sigma\, c_i z_i^2} \tag{6.3.2}$$

which is the general equation for the mean ionic activity coefficient for ions of any valence in any solution whose concentration is known. In Eq. (6.3.2) the $z$'s represent the valence of the ions (positive for negative ions). Introducing numerical values of the constants, we obtain, for uniunivalent electrolytes in water at 25°C,

$$\log f_\pm = -0.506 \sqrt{c} \tag{6.3.3}$$

This equation has been verified in a number of cases as a *limiting law;* that is, as an equation to which the data approach more and more closely as the concentration is lowered.

If we do not consider the ions point charges, but consider them rigid spheres, with the distance of closest approach between ions designated by $a$ (ionic diameter), the equation for the activity coefficient becomes

$$\ln f_\pm = -\frac{z_+ z_- \epsilon^2}{2DkT} \frac{\kappa}{1 + \kappa a} \tag{6.3.4}$$

Fowler and Guggenheim[7] point out that even at concentrations as low as 0.001 molar, the value of $\kappa a$ of Eq. (6.3.4), with $a$ equal to $3 \times 10^{-8}$, is about 0.03, and therefore not negligible with respect to unity. They recommend testing the Debye theory by suitably adjusting the parameter $a$ and then seeing if the chosen values of $a$ are physically reasonable. This they have done, using the freezing-

[7] Fowler and Guggenheim, *op. cit.*, p. 401.

point lowering data of Hovorka and Rodebush.[8] They find that they can reproduce the freezing-point data to 0.0001°C up to all values of the ionic strength equal to 0.01 if they use the values of $a$ for the different salts given in Table 6.1.

TABLE 6.1

VALUES OF $a$ REQUIRED TO BRING AGREEMENT BETWEEN THE DEBYE-HÜCKEL THEORY AND EXPERIMENT

| *Electrolyte:* | KCl | $CsNO_3$ | $K_2SO_4$ | $Ba(NO_3)_2$ | $MgSO_4$ | $CuSO_4$ | $La_2(SO_4)_3$ |
|---|---|---|---|---|---|---|---|
| $a$ in Å | 3.8 | 3.0 | 3.0 | 2.1 | 3.0 | 2.2 | 3.0 |

In the previous paragraph we used the expression ionic strength. This function, originally invented by G. N. Lewis[9] and represented by the symbol $\mu$, is defined as

$$\mu = \tfrac{1}{2} \sum_i m_i z_i^2 \tag{6.3.5}$$

where $m_i$ is the molality of the $i$th ion (any selected ion) and $z_i$ is its valence. It is one of the great achievements of the Debye interionic attraction theory that a theoretical significance was given to the ionic strength, inasmuch as this function appears in all equations of the Debye theory. In terms of the ionic strength the Debye $\kappa$ function is given by the equation

$$\kappa^2 = \frac{8\pi\epsilon^2 N}{1000 DkT}\mu \tag{6.3.6}$$

(More correctly for use with the Debye theory we should use here ionic strengths defined in terms of molarity rather than molality; however, for water as a solvent in dilute solution, the correction term to be applied to (6.3.6) is $\rho_0$, the density of the water, which is very close to unity; hence the difference between the two concentration units is negligible for aqueous solutions at low concentrations. Another relation between $c_i$ and $m_i$ is

$$c_i = m_i\left(\rho - \frac{c_i M}{1000}\right) \tag{6.3.7}$$

where $M$ is the molecular weight of the solute and $\rho$ is the density of the solution).

Other successes of the Debye theory may be listed as follows: The influence of valence type is correctly given in Eq. (6.3.2) by the

[8] F. Hovorka and W. H. Rodebush, *J. Am. Chem. Soc.*, **47**, 1614 (1925).
[9] G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

absolute value of the product of the valence of the positive and negative ion of the electrolyte under consideration. The influence of changing solvent is given in the Debye theory by the factor $D$, representing the dielectric constant of the solvent. The temperature also enters into the equation for the activity coefficient. The Debye theory has been applied successfully to interpretation of the electric conductance and viscosity of electrolytes, heats of dilution, and osmotic coefficients.[10]

## 6-4. *Extensions of the limiting law*

As already remarked, the mathematical derivation of the limiting law may be extended to consideration of the finite size of the ions. When this is done, the potential due to the ionic atmosphere at the distance $r$ from the selected ion becomes

$$\psi_{II} = \frac{z_i\epsilon}{Dr}\left(\frac{e^{\kappa a_i}}{1 + \kappa a_i}e^{-\kappa r} - 1\right) \tag{6.4.1}$$

Now, instead of allowing $r$ to approach zero, we let it approach $a_i$ and obtain for $\psi_i$ the expression

$$\psi = -\frac{z_i\epsilon}{D}\cdot\frac{\kappa}{1 + \kappa a_i} \tag{6.4.2}$$

Equation (6.3.4) for the activity coefficient readily follows.

Another extension of the Debye theory is to consider higher terms in the series expansion of the exponentials of (6.2.4). This has been done for terms of the third and fifth order by Gronwall, La Mer, and Sandved and by La Mer, Gronwall, and Greiff,[11] but the results are rather complicated and will not be discussed further here.

## 6-5. *Statistical theory of ion association*

An interesting application of the Maxwell-Boltzmann distribution law was made in 1926 by Bjerrum,[12] who showed that on the basis of Coulomb's law one could expect two ions to associate if they approach closer than a certain minimum distance where their electric

[10] See *The Physical Chemistry of Electrolytic Solutions*, 2d ed., by H. S. Harned and B. B. Owen, Reinhold Publishing Corporation, New York, 1950, for an exhaustive discussion of all aspects of the Debye theory as applied to electrolytes.

[11] T. H. Gronwall, V. K. La Mer, and K. Sandved, *Physik Z.*, **29,** 358 (1929); V. K. La Mer, T. H. Gronwall, and L. J. Greiff, *J. Phys. Chem.*, **35,** 2245 (1931).

[12] N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, **7**, No. 9 (1926).

energy of association becomes greater than $2kT$. The energy of electric interaction per mole between two ions designated by $i$ and $j$ is given according to Coulomb's law by the expression

$$E_{ij} = \frac{z_i z_j \epsilon^2}{Dr} N_a \tag{6.5.1}$$

The number of ions, $dn_j$, say of the $j$-type, in a concentric shell of volume $4\pi r^2\, dr$ at distance $r$ from a selected ion, say of the $i$-type, will be equal to the average concentration of those ions per cubic centimeter

$$\frac{N_a c_j}{1000}$$

where $N_a$ is Avogadro's number and $c_j$ is the concentration of the $j$-ions in moles per liter, multiplied by the Boltzmann factor $e^{-z_i z_j \epsilon^2 N_a / DrRT}$ and by the volume, $4\pi r^2\, dr$, or

$$dn_j = \frac{N_a c_j}{1000} e^{-z_i z_j \epsilon^2 / DrkT} 4\pi r^2\, dr \tag{6.5.2}$$

Equation (6.5.2) could have been obtained from the Boltzmann distribution law in the form expressed by Eq. (5.7.1) by considering that state 1 represents the state of zero electrostatic energy, and $g_1$ and $g_2$ are volume elements in which $n_1$ and $n_2$ ions are found.

Figure 6.5 illustrates the number of ions, $dn_j$, in the volume element $4\pi r^2\, dr$, at a distance $r$ from an $i$-ion as calculated from (6.5.2) for three cases, ions oppositely charged, curve 1; ions uncharged, curve 2; and ions similarly charged, curve 3.

Note that curve 1 passes through a minimum at which point $r$ can be shown to have the value

$$r_{min.} = \frac{z_i z_j \epsilon^2}{2DkT} \tag{6.5.3}$$

From (6.5.3) it can be readily seen that the electrostatic energy required to separate two ions at the distance $r_{min.}$ to infinity is

$$\frac{z_i z_j \epsilon^2}{D r_{min.}} = 2kT \tag{6.5.4}$$

It is Bjerrum's hypothesis that oppositely charged ions that are nearer to each other than the distance $r_{min.}$ may be considered to be

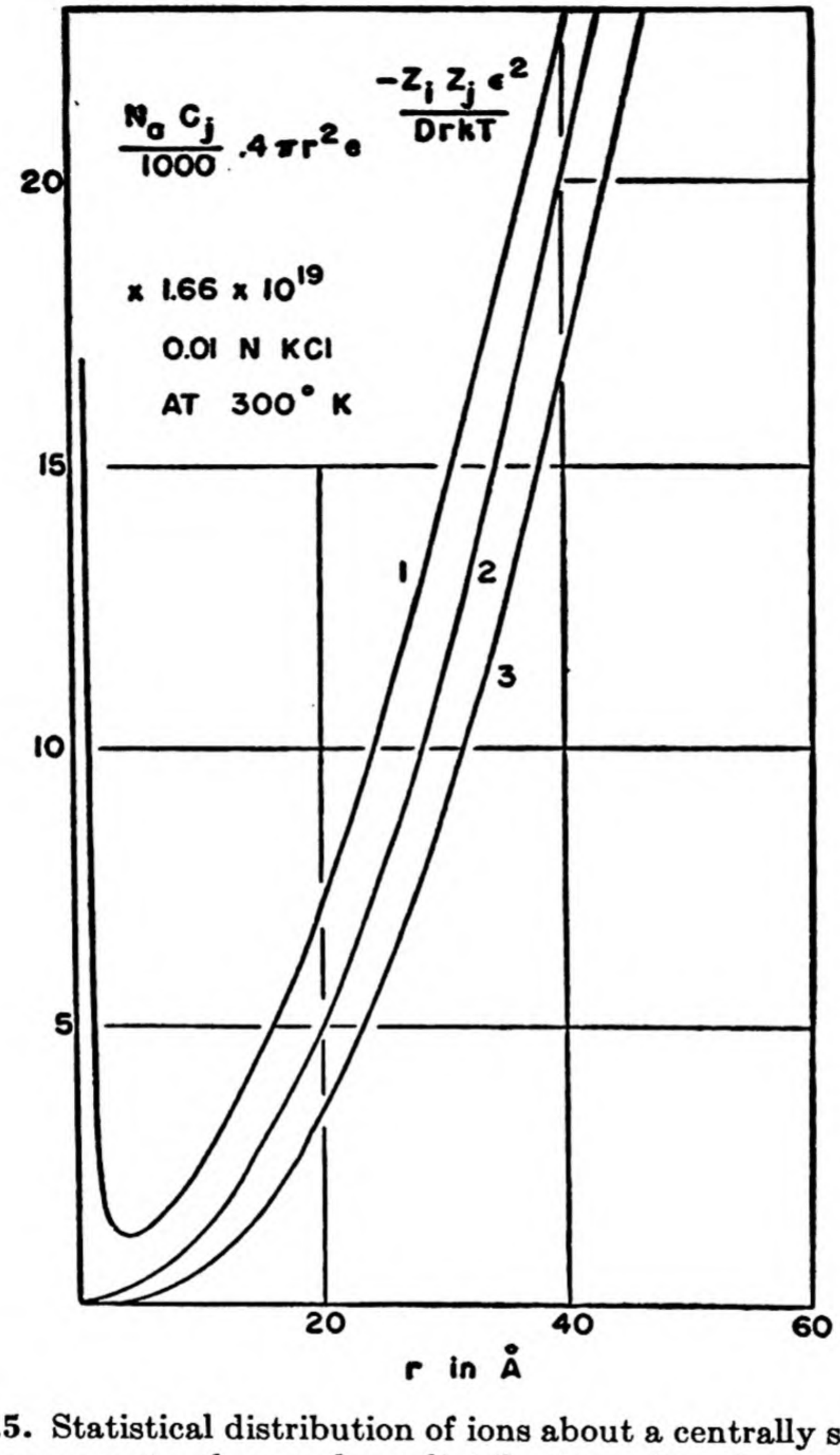



**Fig. 6.5.** Statistical distribution of ions about a centrally selected ion. Curve 2 represents the random distribution of uncharged particles; curve 3 the distribution of ions having the same sign as the centrally selected ion; and curve 1 the distribution of ions having an opposite sign to the centrally selected ion.

associated, because the dissociation energy is four times the average kinetic energy per degree of freedom at the distance $r_{min.}$ and increases greatly at smaller distances. For water at 18°C, $r_{min.}$ calculated from (6.5.3) for oppositely charged univalent ions comes out to be 3.52Å, so that salts whose ionic radii added together are

greater than 3.52Å, KCl for example, have practically no probability of becoming associated.

From Eq. (6.5.1) we see that the smaller the ionic radius, the more highly charged the ions, and the lower the dielectric constant, the higher will be the dissociation energy and the less likely the ionization of the salt.

## PROBLEMS

**1.** Derive an equation similar to (6.2.5) valid for any mixture of electrolytes of any valence.

**2.** Prove that (6.2.12) follows from (6.2.7).

**3.** Demonstrate that (6.2.15) is a solution of (6.2.13).

**4.** When a finite size of the ions is considered, the equation for the potential due to the ionic atmosphere must now be the potential due to the atmosphere at a distance $a$, rather than at $r = 0$ from the location of the central ion. It is also necessary that the field $\partial\psi/\partial r$ be continuous at the distance of closest approach $a$, which will be true if the field due to the ion and its atmosphere, $\partial\psi_{I+II}/\partial r$ equals the field due to the ion itself $\partial\psi_I/\partial r$ at $r = a$, or in other words, that $\partial\psi_{II}/\partial r$ be equal to zero at $r = a$. This means that we need to re-evaluate the constant $A$ of the solution to the fundamental differential equation.

(a) Find $\psi_{II}$ in terms of $A$; i.e., solve for $\psi_{II}$ before evaluating $A$.

(b) Find $\partial\psi_{II}/\partial r$ at $r = a$, and after setting the result equal to zero, evaluate $A$ and so check Eq. (6.4.2).

**5.** Prove that

$$\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-} = z_+ z_-$$

where $\nu_i$ represents the number of ions of the $i$th kind that one molecule of the salt dissociates into.

**6.** Using the standard values of various constants given in Appendix Table 1, calculate

(a) the effective thickness of the ionic atmosphere in 0.01 and $0.1N$ KCl.

(b) the value of $\psi_{II}$ at $r = a$ for KCl (using the value of $a$ given in Table 6.1) in $0.1N$ KCl and compare the value of $\psi_{II}$ with the value of $\psi_I$ at the same location.

temperatures, except in the atomic bomb at the moment of explosion, the nuclei are not excited thermally to energy states above their normal or ground state. Many nuclei, however, possess a spin in their lowest state; this spin of the electrically charged nucleus produces a magnetic field that will interact with an externally applied field, causing an orientational quantization of the nucleus with a wave function for each quantization. In the absence of the field, these oriented states are not detectable, but exist nevertheless and give to the nucleus a weight $g_n$. The value of $g_n$ is computed from the equation

$$g_n = 2i + 1 \tag{10.1.1}$$

where $i$ is the nuclear spin, 1/2 for hydrogen (protium) and 1 for deuterium.

In most systems of chemical interest it is unnecessary to consider nuclear spin weights because: (a) they contribute nothing to the energy or heat capacities; (b) although contributing an additive term to the free energy and entropy, this additive term is unchanged in a chemical reaction and cancels in the calculation of the free energy and entropy changes of the reaction. The convention has been adopted, therefore, of neglecting nuclear spin weights in the partition function and nuclear spin contributions to the free energy and entropy.

However, there is one important exception to the neglect of nuclear spins in the statistical thermodynamic theory; namely, in the heat capacity and entropy of ordinary hydrogen. Because neither the proton nor the deuteron has a zero nuclear spin and because the rotational energy states have to be treated according to the quantum theory up to 300°K, we cannot ignore the nuclear spin factor in interpreting thermodynamic data for hydrogen and deuterium. Without a knowledge of nuclear spins the observed entropy of hydrogen would continue to be a profound puzzle.

In the case of a heteronuclear molecule (a molecule composed of unlike atoms) there are $g_a$ nuclear wave functions for atom $a$ and $g_b$ nuclear wave functions for atom $b$, one for each oriented state. These wave functions can combine in $g_a g_b$ ways giving $g_a g_b$ molecular wave functions of the type

$$\psi_r(a)\psi_s(b)$$

The rotational partition function of the heteronuclear diatomic molecule taking into consideration nuclear spins is therefore

$$Q_{rot} = g_a g_b \sum_{j=0,1,2,3,\ldots} (2j+1) e^{-j(j+1)\beta h^2/8\pi^2 I} \qquad (10.1.2)$$

Turning now to a molecule with identical nuclei, a homonuclear molecule such as molecular hydrogen or deuterium, we find that the proton can have the orientational spin wave functions

$$\psi_{-1/2}, \qquad \psi_{+1/2}$$

and the deuteron $\psi_{-1}, \qquad \psi_0, \qquad \psi_{+1}$

The hydrogen molecule, because of symmetry in the nuclei, has the following nuclear spin wave functions:

$$\psi_{1/2}(a)\psi_{1/2}(b)$$
$$\psi_{-1/2}(a)\psi_{-1/2}(b)$$

symmetrical in the nuclei, or $g_n$ such functions. By the expression "symmetrical in the nucleus" we mean that the wave function does not change sign if the nuclei are interchanged. Now in addition to the above wave functions, which are satisfactory functions for the Schrödinger wave equation, we have the following solutions:

$$\psi_{1/2}(a)\psi_{-1/2}(b) + \psi_{-1/2}(a)\psi_{+1/2}(b)$$
$$\psi_{1/2}(a)\psi_{-1/2}(b) - \psi_{-1/2}(a)\psi_{+1/2}(b)$$

where the first is symmetric and the second an antisymmetric wave function. In general, there are $\frac{1}{2}g_n(g_n - 1)$ antisymmetric and $\frac{1}{2}g_n(g_n + 1)$ total symmetric wave functions. The sum of $\frac{1}{2}g_n(g_n - 1)$ and $\frac{1}{2}g_n(g_n + 1)$ is just $g_n^2$, which is the number of wave functions of a heteronuclear molecule containing two nuclei of equal $g_n$ value.

In the case of deuterium, the situation is a little more complicated, since there are 6 symmetric and 3 antisymmetric functions, or 9 in all, as follows:

$$\psi_1(a)\psi_1(b)$$
$$\psi_0(a)\psi_0(b)$$
$$\psi_{-1}(a)\psi_{-1}(b)$$
$$\psi_1(a)\psi_{-1}(b) + \psi_{-1}(a)\psi_{+1}(b)$$
$$\psi_0(a)\psi_{-1}(b) + \psi_{-1}(a)\psi_0(b)$$
$$\psi_{+1}(a)\psi_0(b) + \psi_0(a)\psi_{+1}(b)$$

symmetric functions, and

$$\begin{aligned}
&\psi_1(a)\psi_{-1}(b) - \psi_{-1}(a)\psi_1(b)\\
&\psi_0(a)\psi_{-1}(b) - \psi_{-1}(a)\psi_0(b)\\
&\psi_{+1}(a)\psi_0(b) - \psi_0(a)\psi_{+1}(b)
\end{aligned}$$

antisymmetric functions. The total is 9, which is equal to $g_n^2$, since $g_n$ for deuterium is 3.

One of the fundamental discoveries resulting from the application of nuclear symmetry studies during the 1930's was that nuclei of odd mass number (1, 3, 5, etc.) have accessible states that are antisymmetrical in the nuclei, while the states accessible to nuclei of even mass number are only those symmetrical in the nuclei. We have to consider the symmetry properties, with respect to the nuclei, of the wave functions for translation, rotation, and vibration of the molecule. The wave function for translation depends only on the center of mass of the molecule, and is independent of the relative position of the two nuclei within the molecule. The translational wave function is always symmetric. The rotational wave functions are symmetric for even quantum numbers, 0, 2, 4, etc., and antisymmetric for odd quantum numbers, 1, 3, 5 etc. For example, the rotational wave function does not change sign if the angle $\varphi$ is increased by $\pi$ for $j$ even, 0, 2, 4, 6, etc., but does change sign when $\varphi$ is increased by $\pi$ for $j$ odd. The vibrational wave function for the ground state of a harmonic oscillator is symmetric. Since we are dealing with molecules at low temperatures we are not concerned with higher vibrational states, and therefore do not have to consider the symmetry properties of the nuclei with respect to vibration. For the ground electronic state of a molecule containing an even number of electrons, the electronic orbital wave function is symmetric in the nuclei; the electronic spin wave function is also symmetric in the nuclei, because the nuclear coordinates do not affect the spin wave function.

For homonuclear molecules whose nuclei have odd mass numbers, the antisymmetric nuclear wave functions have to be combined with symmetric rotational wave functions or *vice versa*, so that the combined wave function is antisymmetric. This means that the rotational partition function for homonuclear molecules having nuclei of odd mass number, $H_2$ for example, takes the form

$$Q_{rot.} = \tfrac{1}{2}g_n(g_n - 1)\sum_{j=0,2\ldots}(2j+1)e^{-j(j+1)\beta h^2/8\pi^2 I} + \tfrac{1}{2}g_n(g_n+1)\sum_{j=1,3,5\ldots}(2j+1)e^{-j(j+1)\beta h^2/8\pi^2 I} \qquad (10.1.3)$$

For homonuclear molecules having nuclei of even mass numbers such as deuterium, it is necessary to combine symmetrical nuclear wave functions with symmetrical rotational wave functions and antisymmetric with antisymmetric, so that the over-all wave function is symmetric; thus

$$Q_{rot.} = \tfrac{1}{2}g_n(g_n+1)\sum_{j=0,2\ldots}(2j+1)e^{-j(j+1)\beta h^2/8\pi^2 I} + \tfrac{1}{2}g_n(g_n-1)\sum_{j=1,3\ldots}(2j+1)e^{-j(j+1)\beta h^2/8\pi^2 I} \qquad (10.1.4)$$

For heteronuclear molecules we have

$$Q_{rot.} = g_a g_b \sum_{j=0,1,2,3\ldots}(2j+1)e^{-j(j+1)\beta h^2/8\pi^2 I} \qquad (10.1.5)$$

The forms of hydrogen and deuterium for which the nuclear spin wave functions are symmetric are called *ortho*-hydrogen and *ortho*-deuterium, while the forms of hydrogen and deuterium with antisymmetric nuclear spin wave functions are called *para*-hydrogen and *para*-deuterium. *Para*- and *ortho*-hydrogen and deuterium can also be described by saying that the *para* forms have nuclei with anti-parallel spins and *ortho* forms have nuclei with parallel nuclear spins. This statement is only approximately correct.

Referring to Eqs. (10.1.3) and (10.1.4) it should be noted that when the spin of the nucleus is zero, resulting in a value of unity for $g_n$, the requirements of nuclear symmetry lead to the complete absence of alternate rotational states of a homonuclear molecule. This is the quantum theory analog of a symmetry number equal to 2; the disappearance of the alternate rotational states has been completely verified spectroscopically for such homonuclear molecules with zero nuclear spin as $O_2^{16}$. For homonuclear molecules with nuclei of nonzero spin like hydrogen, the sum of the two terms in Eqs. (10.1.3) or (10.1.4) is effectively only half the single term of Eq. (10.1.5); here again we have the quantum theory analog of the symmetry number.

The rotational contribution to the heat capacity of a gas is given by the expression

$$C_{rot.} = R \frac{d}{dT} T^2 \frac{\partial \ln Q_{rot.}}{\partial T}$$

For a heteronuclear molecule such as HD we have

$$Q_{rot.} = g_a g_b \sum_{j=0,1,2} (2j + 1) e^{-\beta j(j+1) h^2/8\pi^2 I}$$

or $$Q_{rot.} = 6(1 + 3e^{-2\beta h^2/8\pi^2 I} + 5e^{-6\beta h^2/8\pi^2 I} + \ldots)$$

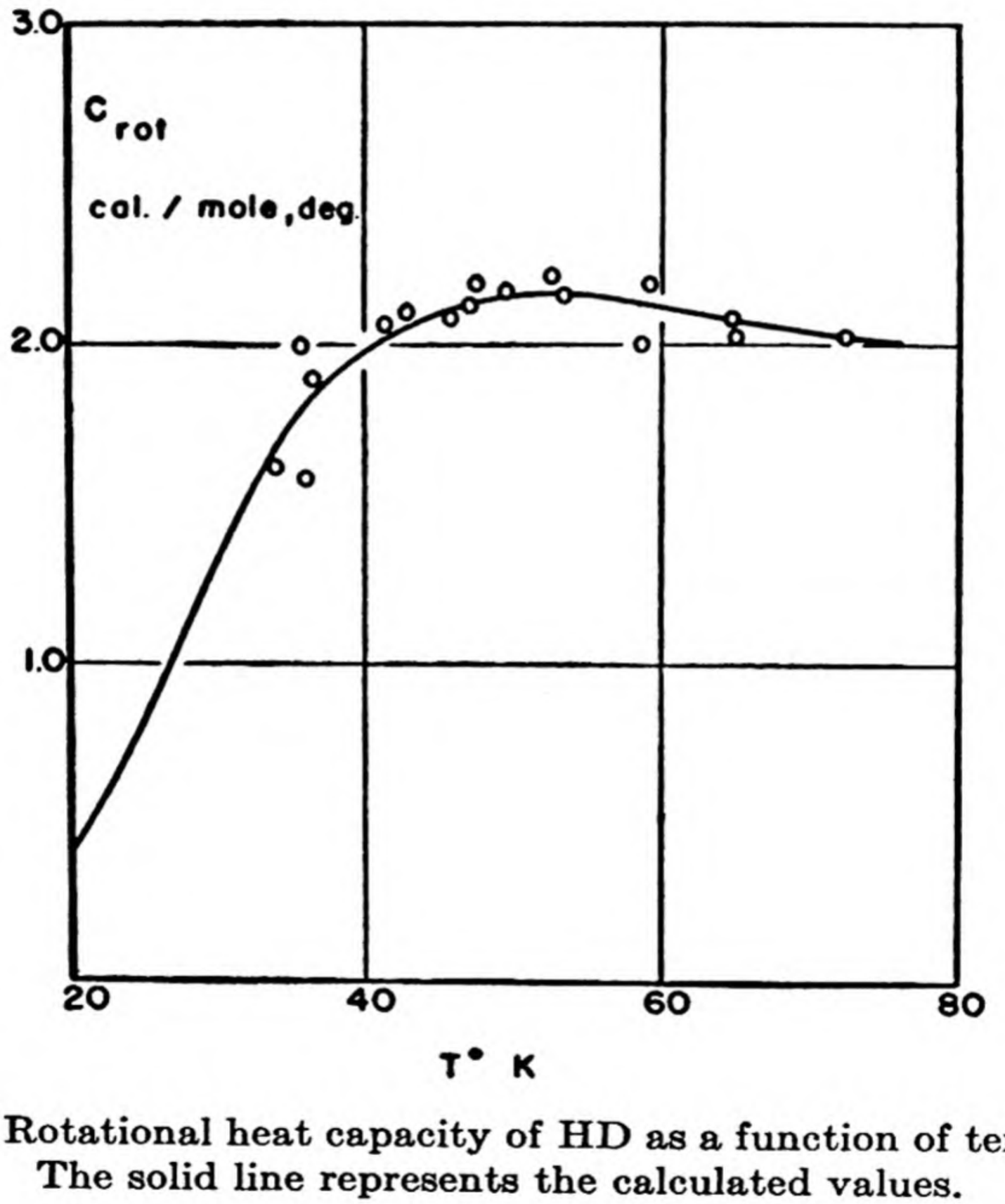



**Fig. 10.1.** Rotational heat capacity of HD as a function of temperature. The solid line represents the calculated values.

In Fig. 10.1, the solid line shows that calculated values of $C_{rot.}$ as a function of the absolute temperature agree well with the experimental data, circles, obtained by Clusius and Bartholomé.[1] Especially convincing is the discovery of the predicted maximum at about 50°K.

[1] K. Clusius and E. Bartholomé, *Z. Elektrochem.*, **40**, 524 (1934).

Since the classical value for the rotational contribution to the heat capacity is 1.987 for a diatomic molecule, it can be seen that the rotational motions of HD become essentially classical above 80°K.

Now the total rotational partition function for $H_2$ might be expected to be

$$Q_{rot.} = \sum_{j=0,2,4\ldots}^{\infty} (2j+1)e^{-j(j+1)\beta h^2/8\pi^2 I} + 3\sum_{j=1,3,5\ldots}^{\infty} (2j+1)e^{-j(j+1)\beta h^2/8\pi^2 I} \qquad (10.1.6)$$

Rotational heat capacities calculated by Hund,[2] using (10.1.6), bore no relation at all to the observed. This apparent anomaly was solved by Dennison,[3] who made the suggestion that *ortho*-hydrogen usually fails to be converted to *para*-hydrogen as the temperature is lowered below 300°K, with the result that the equilibrium ratio of *ortho*- to *para*-hydrogen is *not* established in accordance with Eq. (10.1.6). It will be noted by studying Eq. (10.1.6) that as the temperature approaches 0°K, *ortho*-hydrogen should be converted to *para*-hydrogen, inasmuch as all molecules should be found in the lowest rotational state with $j$ equal to zero at the absolute zero of temperature. In other words, although the ratio of *para*- to *ortho*-hydrogen at room temperature is only one to three, at the absolute zero of temperature the hydrogen should be all *para*. However, for the conversion *ortho*- to *para*-hydrogen to occur, it is necessary either that molecular hydrogen dissociate into atoms and then recombine according to the equilibrium distribution in all the states enumerated in (10.1.6) or that a paramagnetic substance be present whose moment interacts with the magnetic moment associated with the spins of the hydrogen nuclei to a sufficient extent to produce the conversion *ortho* to *para*. In ordinary hydrogen gas, interchanges between the symmetric and antisymmetric states do not occur appreciably in the time of an experiment (even over weeks at low temperatures); hence one must consider hydrogen as a metastable mixture of three parts of *ortho*- to one part of *para*-hydrogen. As can be seen from (10.1.6) the high temperature ratio of *ortho* to *para* is 3:1. We must calculate the rotational heat capacity of hydrogen from the equation

[2] F. Hund, *Z. Physik*, **42**, 93 (1927).
[3] D. M. Dennison, *Proc. Roy. Soc.*, London, **A115**, 483 (1927).

$$C_{rot.} = \tfrac{1}{4}C_{rot.}^{para} + \tfrac{3}{4}C_{rot.}^{ortho} \qquad (10.1.7)$$

and treat hydrogen as if it were a mixture of two separate gases. When this is done, exceptionally good agreement is obtained between the calculated and observed values as illustrated in Fig. 10.2.

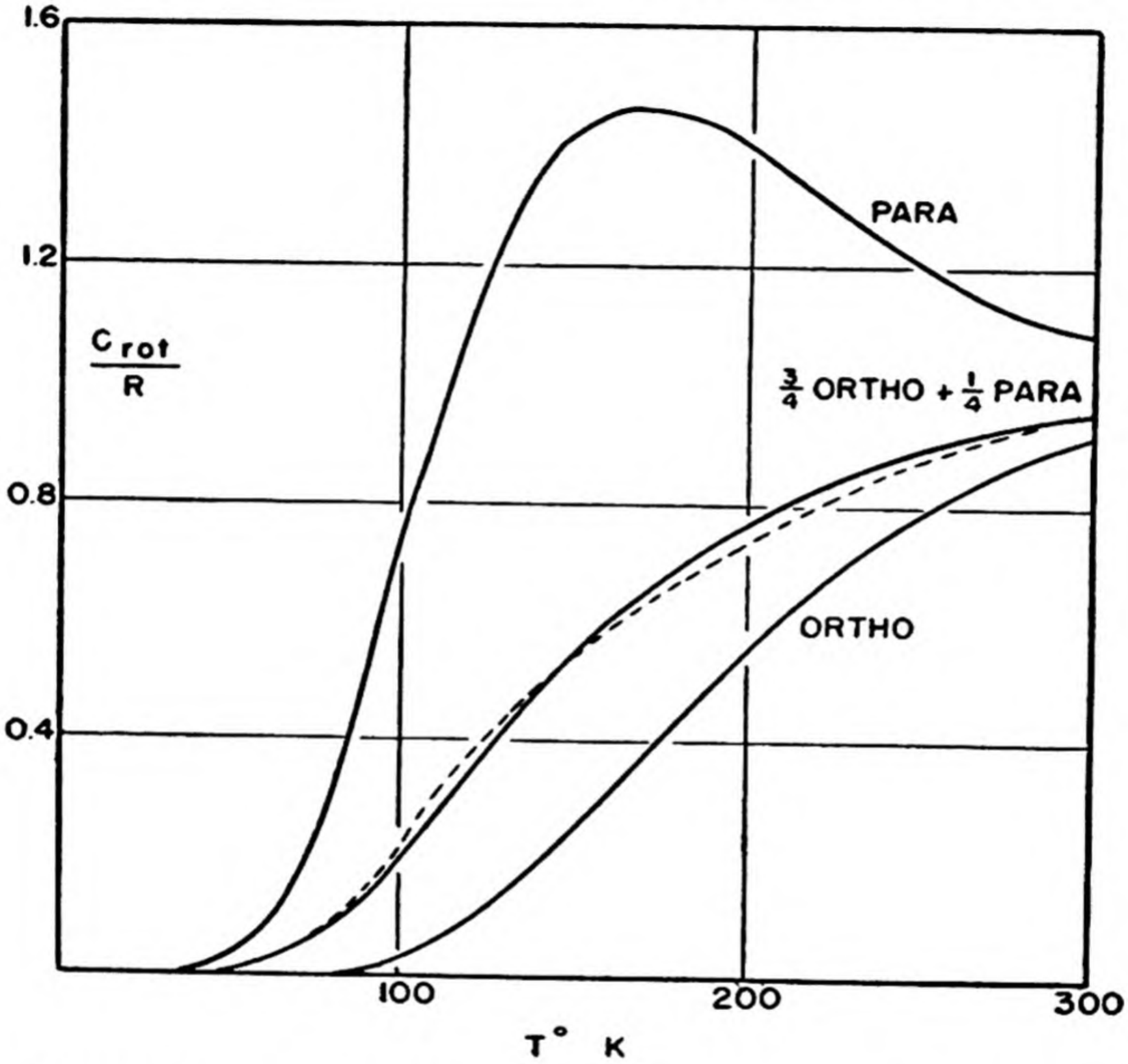



**Fig. 10.2.** Calculated rotational heat capacity of *ortho* and *para*-hydrogen and of the high temperature equilibrium mixture, compared with the experimentally observed values shown by the dashed line.

Note that at temperatures above 300°K, the heat capacity due to rotation approaches the classical value of 2.0 cal./deg. mole.

The calculation of the expected ratio of *ortho*- to *para*-deuterium is given as a problem at the end of the chapter.

The translational contribution to the heat capacity has its expected classical value.

## 10-2. *Heat capacity of hydrogen at high temperatures*

Turning now to the question of the contribution of vibrational motions in the hydrogen molecule to the heat capacity, we have to go to temperatures of 600°K or higher, because $h\nu$ for hydrogen is so

high ($\nu$ is the fundamental mode of vibration), of the order of magnitude of 12,000 cal./mole. A value of $RT$ equal to 12,000 requires a temperature of about 6000°K; thus all the hydrogen molecules will be in their lowest or ground vibrational state up to temperatures of about 600°K, and the upper vibrational states will not become appreciably populated until much higher temperatures are reached, 2000° or 3000°K. At 6000°K, when we might expect the vibrational contribution to the heat capacity to become equal to the classical value, the hydrogen molecule is practically completely dissociated. Thus the hydrogen molecule begins to dissociate, and the energy of dissociation begins to contribute to the heat capacity, at temperatures below the point where the vibrations can be treated according to classical mechanics. This is why we are hardly ever concerned with the classical vibrational partition function.

At temperatures above 300°K, the differences between the symmetrical and antisymmetrical rotational states are negligible, but we cannot use the simple rotational and vibrational partition functions to evaluate the heat capacity because of interaction between rotation and vibration. Instead, the energies of the rotational and vibrational states of the molecule as deduced from the band spectrum of hydrogen are inserted directly into the double sum

$$Q_{vib.}Q_{rot.} = \sum_{v=0}^{\infty} \sum_{j=0}^{\infty} (2j+1)e^{-\beta\epsilon(v,j)} \tag{10.2.1}$$

When (10.2.1) is used in estimating the vibrational and rotational contributions to the heat capacity of hydrogen, excellent agreement is obtained with the experimental data up to 2500°K.

## 10-3. *Heat capacity of diatomic gases*

For gases whose rotational vibrational interaction can be ignored, the equation for the vibrational heat capacity takes the form

$$C_{vib.} = R\left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{(e^{\theta/T}-1)^2} \tag{10.3.1}$$

where

$$\theta = \frac{h\nu}{k} \tag{10.3.2}$$

Questions of nuclear symmetry are of no consequence here because the classical rotational partition function is applicable at all temperatures for which the diatomic gases are gaseous (hydrogen and

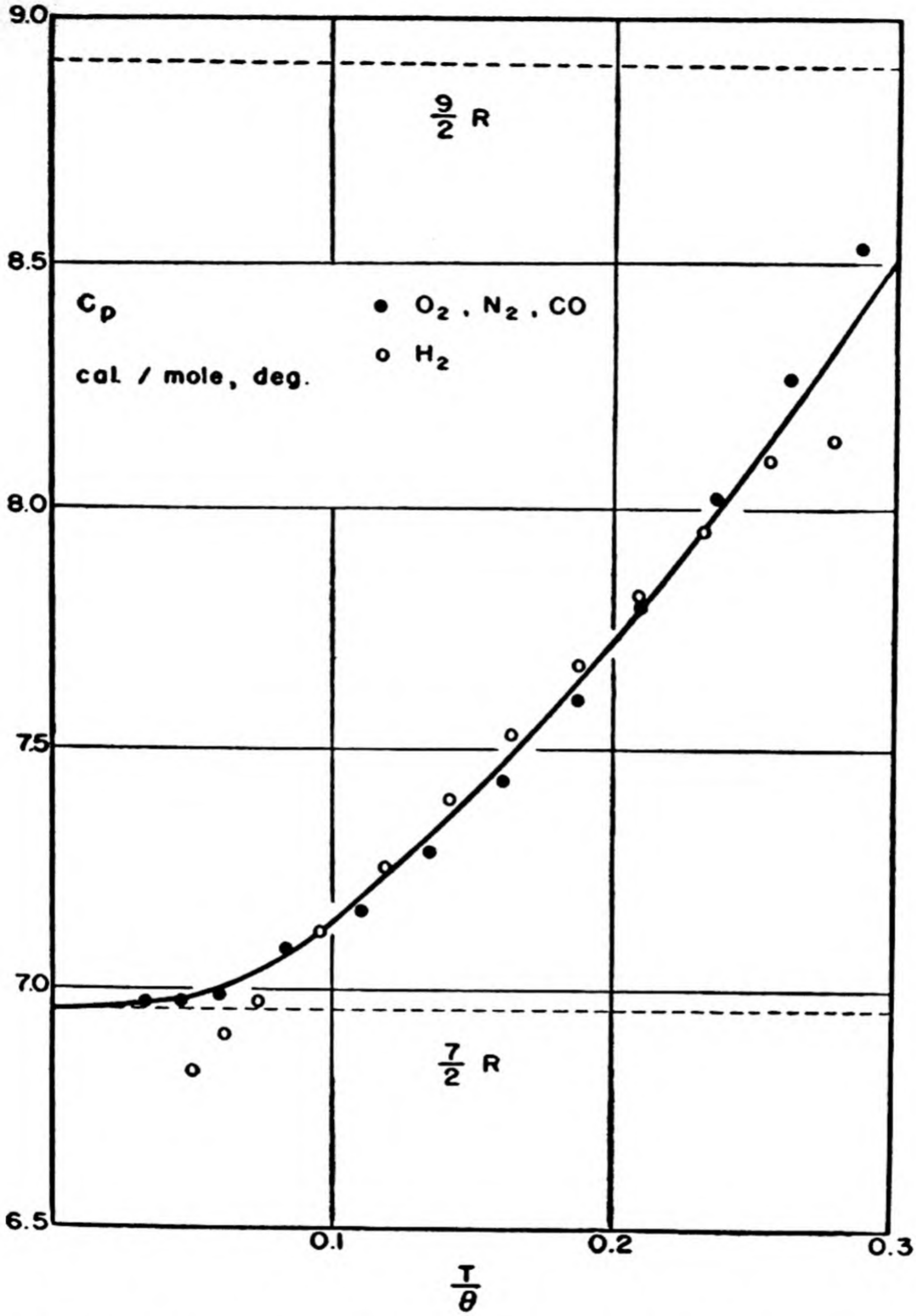



**Fig. 10.3.** Molar heat capacity of $N_2$, $O_2$, and $H_2$ as a function of $T/\theta$.

deuterium excepted, of course). An inspection of Eq. (10.3.1) reveals the fact that all diatomic gases should have the same vibrational contribution to the heat capacity if compared at the same value of $\theta/T$. Such a comparison is illustrated in Fig. 10.3 where the agreement can be seen to be all that is desired.

If the molecule possesses an electronic state that lies close to that of the ground state, as is the case for NO, whose lowest state belongs to a doublet with only about 356 cal./mole separating it from the higher state of the doublet, the electronic contribution to the heat capacity must be considered. The electronic partition function for NO is therefore

$$Q_{elec.} = g_0 + g_1 e^{-\beta\epsilon_1} = 2 + 2e^{-\beta\epsilon_1} \qquad (10.3.3)$$

Each component of the doublet has a statistical weight equal to 2. Such an electronic partition function, when combined with the usual translational and rotational partition functions, yields as the relevant partition function in the temperature range of interest (below room temperature)

$$Q_{NO} = \frac{(2\pi mkT)^{3/2}}{h^3} V \frac{8\pi^2 IkT}{h^2} (2 + 2e^{-\beta\epsilon_1}) \qquad (10.3.4)$$

From (10.3.4) the equation for the heat capacity at constant volume becomes

$$C_v = \frac{5}{2}R + \frac{R(\epsilon_1/kT)^2}{(1 + e^{\epsilon_1/kT})(1 + e^{-\epsilon_1/kT})} \qquad (10.3.5)$$

The second term of the equation has a maximum value of 0.88 when $\epsilon_1/kT$ is equal to 2.4. This corresponds to a temperature of 74°K because of the small value of $\epsilon_1$, and signifies that the heat capacity of NO should *increase* with decrease of temperature near 74°K as the temperature is lowered toward 74°K. Such a rather anomalous behavior of the heat capacity has been discovered by Eucken and d'Or.[4]

In the case of oxygen, the next highest electronic state above the triplet ground state, $^3\Sigma_g$, is the $^1\Delta_g$ state which is doubly degenerate and whose energy is 0.98 e.v., or 22,630 cal./mole. The electronic partition function is

$$Q_{elec.} = 3 + 2e^{-\beta\epsilon_1} \qquad (10.3.6)$$

and begins to contribute detectably to the heat capacity at a temperature of 1750°K. At 2500° its contribution is still small, however.

[4] A. Eucken and L. d'Or, *Gott. Nachr.*, p. 107 (1932).

## 10-4. *Heat capacity of polyatomic gases*

As the complexity of molecules increases, the calculation of the heat capacity becomes even more difficult. Let us consider a relatively simple example, the calculation of the heat capacity of carbon dioxide. Being a triatomic molecule, it has nine degrees of freedom, which, after subtracting 3 for translation and 2 for rotation, leaves 4 degrees of freedom for vibrational motion. From a study of the infrared absorption spectra, Raman spectra, dielectric properties, etc., it is concluded that carbon dioxide is a linear symmetric molecule having three fundamental frequencies[5] of vibration; at 1337,

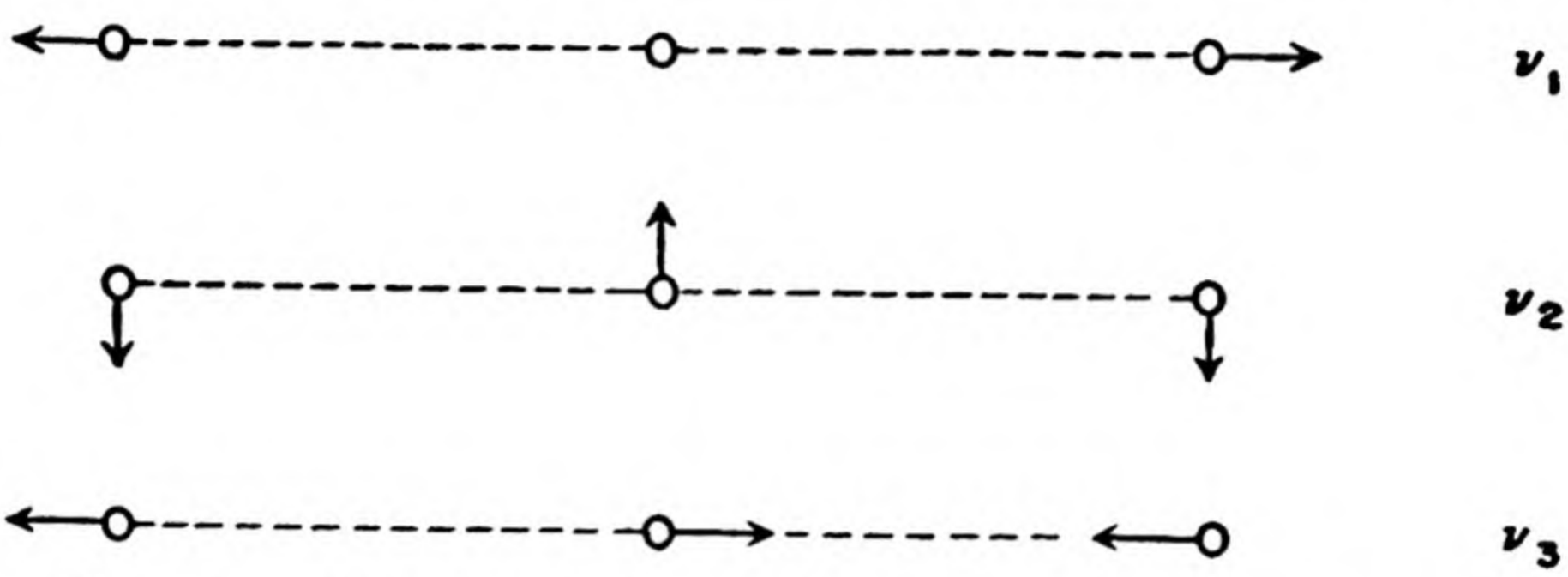



**Fig. 10.4.** Normal modes of vibration of the $CO_2$ molecule.

667.3, and 2349.3 cm.$^{-1}$ ($\nu_1$, $\nu_2$, and $\nu_3$, respectively).[6] The atomic motions that give rise to the frequencies mentioned are pictured in Fig. 10.4. The vibration $\nu_2$ is double degenerate, that is to say, there is another vibration not pictured in Fig. 10.4 that has exactly the same frequency as $\nu_2$ and that results from atomic vibrations in a plane perpendicular to the plane of the paper.

To compute the heat capacity we add to the classical translational and rotational contributions (which are independent of temperature)

$$\tfrac{3}{2}R + \tfrac{2}{2}R$$

the contributions due to the vibrations calculated on the basis of quantum theory from the expression

[5] The unit of energy cm.$^{-1}$ is the reciprocal of the wavelength. When multiplied by the velocity of light, the frequency is obtained; when multiplied by $hc$, the energy in ergs per molecule is obtained.

[6] These frequencies of vibration for $CO_2$ were taken from G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Company, Inc., New York, 1945, Vol. 2, p. 173.

$$\sum_s R\left(\frac{h\nu_s}{kT}\right)^2 \frac{e^{h\nu_s/kT}}{(e^{h\nu_s/kT}-1)^2}$$

where the summation is over all four fundamental modes of vibration.

Turning now to a molecule containing 5 atoms, $CH_4$, its 15 degrees of freedom can be listed as follows:

| | |
|---|---|
| translational: | 3 |
| rotational: | 3 |
| vibrational: | |
| 2 triply degenerate | 6 |
| 1 doubly degenerate | 2 |
| 1 single mode | 1 |
| total | 15 |

Thus we have to determine the frequency of 4 fundamental modes of vibration. In the assignment of the measured frequencies to different modes, the following principles might be briefly mentioned:

1. Vibrations along bond axes involve the greatest energies and greatest frequencies of vibration.

2. Bending or twisting oscillations usually have low frequencies.

3. If the vibration produces no change in the electric moment of the molecule, the vibration will be inactive (unobserved) in the infrared.

4. Usually when the frequency is inactive in the infrared it is active in the Raman spectrum and vice versa.

The tetrahedral structure of $CH_4$ is brilliantly confirmed by a study of the nature of the infrared and Raman spectra. For example, only molecules of cubic symmetry (only tetrahedral molecules) do not exhibit rotational Raman spectra. In agreement with this observation, $CH_4$ also does not exhibit rotational Raman spectra.

The $\nu_1$ frequency of methane results from a motion of the hydrogen atoms in and out along the direction of the valence bonds, with the carbon atom remaining stationary; since the symmetry of the molecule is not changed by this vibration, there is no production of an electric moment; the vibration consequently cannot be observed in the infrared, but only in the Raman spectrum. Because of the large force constants for this vibration along the bond direction, the frequency is relatively high, and vibrational states above the ground state are not populated sufficiently for this mode of vibration to contribute to the heat capacity at room temperature.

The $\nu_3$ vibration also contributes nothing to the heat capacity because of its high value; it is triply degenerate since the vibrations are orthogonal to one another and are linearly independent. The central carbon atom can be thought of as vibrating along the three Cartesian axes, $x$, $y$, $z$, for the three vibrations. The hydrogen atoms then move in an opposite direction parallel to each other in such a way as to maintain unchanged the center of gravity. These motions produce an electric moment in the molecule so that its triply degenerate frequency is observed in the infrared.

The two frequencies that do contribute to the specific heat at room temperature are the $\nu_2$ and $\nu_4$ frequencies; the first is a doubly degenerate frequency, and the second is a triply degenerate frequency. These frequencies belong to bending or twisting motions of the hydrogen atoms (the carbon atom remains stationary for the $\nu_2$ and $\nu_4$ modes of vibration), and involve, therefore, low enough vibrational energies so that they contribute to the heat capacity at room temperature. The doubly degenerate vibration $\nu_2$ results from a motion of the hydrogen atoms at right angles to the C—H bond in such a way that the molecule remains electrically symmetrical. This frequency is indirectly calculated from Raman bands that are combinations of $\nu_2$ and $\nu_3$, or $\nu_2$ and $\nu_4$, and is not known so accurately as the other frequencies.

The frequency with the lowest value, the triply degenerate $\nu_4$ frequency, produces an electric moment in the molecule because two hydrogen atoms move toward each other along an imaginary line connecting them while the other two move away from each other along their H—H direction. There are three possible independent motions of this type.[7] The numerical values of the frequencies and other relevant data are collected in Table 10.1.

TABLE 10.1

HEAT CAPACITY OF METHANE AT 300°K

| *Frequency classification* | *Spectral type* | *Frequency* (cm.$^{-1}$) | $h\nu/k$ (°K) | $C_{vib.}$ (300°K) | *Degeneracy* | $C_{vib.}$ *total* (300°K) |
|---|---|---|---|---|---|---|
| $\nu_1$ | R. | 2914.2 | 4170 | 0 | 1 | 0 |
| $\nu_2$ | R. | 1526 | 2180 | $0.037R$ | 2 | $0.074R$ |
| $\nu_3$ | R. and I.R. | 3020.3 | 4320 | 0 | 3 | 0 |
| $\nu_4$ | R. and I.R. | 1306.2 | 1870 | $0.077R$ | 3 | $0.231R$ |

[7] In Herzberg, *op. cit.*, these motions are pictured in Fig. 41, p. 100.

The total molal heat capacity at constant pressure $C_p$ for methane at 300°K is therefore

$$C_p = \underset{trans.}{\tfrac{3}{2}R} + \underset{rot.}{\tfrac{3}{2}R} + \underset{vib.}{0.305R} + R$$
$$= 4.035R = 8.56 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

The observed value at 300°K is 8.58 cal. mole$^{-1}$ deg.$^{-1}$, which is in excellent agreement with the calculated value.

The above detailed example of the calculation of the heat capacity of the polyatomic gas methane is sufficient, perhaps, to indicate the necessary procedure. In addition to the types of motion considered, we shall need to allow for internal rotation of molecules, such as rotation of one methyl group in ethane with reference to the second. The methods for treating this problem will be considered later. We shall not discuss in this book the influence of van der Waals forces or the influence of deviation from perfect gas behavior on the heat capacity of gases.

## 10-5. *The specific heat theory of Einstein for solids*

We now turn to consideration of the specific heat of crystalline monatomic solids. These substances represent an ideal state of matter in a condensed form just as gases at low pressure represent an ideal state of matter in an expanded form. Because of the symmetry and simplicity of crystalline solids, equations can be derived that describe their behavior. In particular, we have valuable theories of the heat capacity of solids.

In elementary chemistry, the student is taught to estimate atomic weights of elements whose valence is unknown, by means of the law of Dulong and Petit. This law states that the product of the atomic weight and the specific heat is a constant, near to 6; or mathematically,

$$c_p \cdot (\text{at. wt.}) = 6 \qquad (10.5.1)$$

At that stage in his scientific development, the student knows too little about physics or physical chemistry to understand the significance of the law represented by Eq. (10.5.1). We shall now proceed to derive the law and to delineate the conditions under which it is valid.

Imagine each atom to be executing linear harmonic oscillations about an equilibrium position in the crystalline solid. The motions

can be resolved into components along the $x$, $y$, and $z$ axes of a Cartesian coordinate system. In other words, the atom has three degrees of freedom. For motion along one of the axes, the energy is given by the equation

$$\epsilon = \frac{p^2}{2\mu} + \frac{(2\pi\nu\mu)^2}{2\mu} q^2 \tag{10.5.2}$$

The expression (10.5.2) leads to the expression for the classical vibrational partition function (for the three degrees of freedom)

$$Q_{vib.} = \left(\frac{kT}{h\nu}\right)^3 \tag{10.5.3}$$

or

$$C_v = 3R \tag{10.5.4}$$

As the gas constant $R$ is equal nearly to 2 cal. mole$^{-1}$ deg.$^{-1}$, and as $C_v$ is equal to the specific heat at constant volume multiplied by the atomic weight, we see the fundamental theoretical significance of the law of Dulong and Petit.

However, if the gram atomic heat capacity of the metals is plotted as a function of the absolute temperature as in Fig. 10.5, we see that the atomic heat capacity of all metals falls below the classical value of $3R$ at temperatures characteristic of the metal, and that all atomic heat capacities approach zero at the absolute zero of temperature. Obviously, the law of Dulong and Petit is valid only above certain temperatures, or in the language of statistical thermodynamics, it is valid only at temperatures sufficiently high for the classical vibrational partition function to be valid. The heavier the metal atom and the weaker the forces holding the atoms together, as in the case of lead, the lower the temperature at which the classical vibrational partition function is valid. In the case of carbon in the form of diamond we have the opposite situation, namely, light atoms and strong valence forces binding the crystal together, so that even at room temperature, the atomic heat capacity of carbon is still far below the theoretical value of $3R$.

If the temperature becomes too great, the deviations from harmonic oscillations become significant, and Dulong and Petit's law is no longer valid. We have also not taken into consideration possible electronic contributions to the heat capacity, which in the case of certain transition metals are significant.

It was not until the advent of the quantum theory that an inkling was obtained of the cause for the large discrepancy between the measured heat capacity and the law of Dulong and Petit. Einstein in 1907 suggested that the atoms in the crystal were oscillating with frequencies equal for all atoms and with energies that were quan-

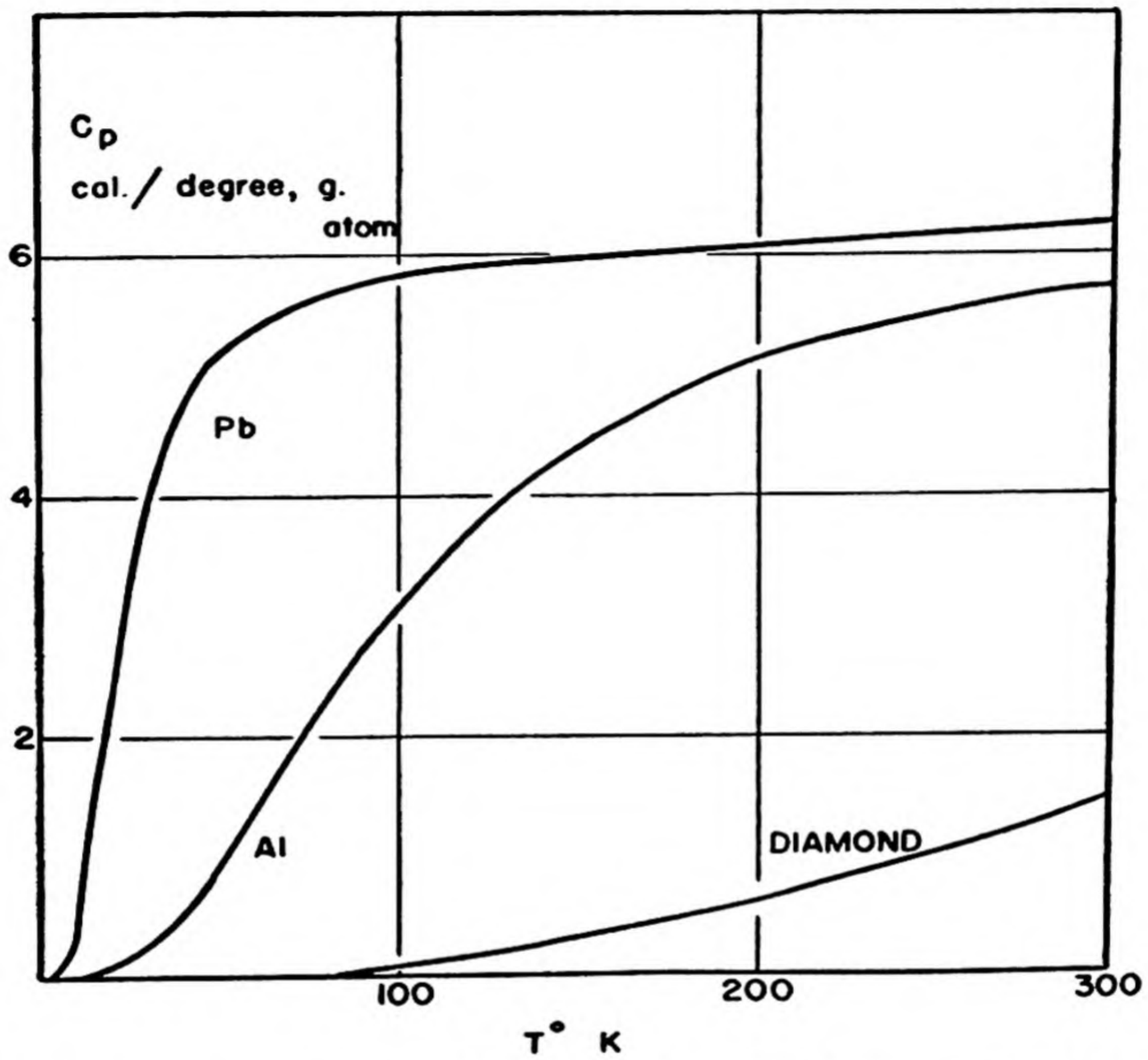



**Fig. 10.5.** Atomic heat capacities of lead, aluminum, and carbon in the form of diamond.

tized. Thus, when heat is added to the crystal, the atoms acquire energy, not continuously as in the classical theory, but in increments such that the energy of any one oscillation at any one time increases by an amount $h\nu$. In fact, modern theory tells us that the energy can be expressed by

$$\epsilon_{vib.} = (v + \tfrac{1}{2})h\nu \tag{10.5.5}$$

where $\frac{1}{2}h\nu$ is zero point energy, and $\epsilon_{vib.}$ is the energy for one atom for one degree of freedom.

The equation for the heat capacity is readily derived as soon as (10.5.5) is accepted as the energy of the oscillator per degree of freedom. We could find the partition function, which would be equal

to that already found, or we can proceed in the following way. We can determine the average energy of the oscillator as a function of the temperature; after differentiating with respect to the temperature and multiplying by $3N$, the gram atomic heat capacity is obtained. Thus, the average energy is defined by the usual statistical thermodynamic equation

$$\bar{\epsilon} = \frac{\sum_{v=0}^{\infty} (v + \frac{1}{2}) h\nu e^{-\beta(v+1/2)h\nu}}{\sum_{v=0}^{\infty} e^{-\beta(v+1/2)h\nu}} \tag{10.5.6}$$

Because $h\nu$ is a constant, independent of $v$ and $T$, Eq. (10.5.6) can be rearranged to give

$$\bar{\epsilon} = \frac{1}{2} h\nu + h\nu \frac{\sum_{v=0}^{\infty} v e^{-\beta v h\nu}}{\sum_{v=0}^{\infty} e^{-\beta h\nu}} \tag{10.5.7}$$

Expanding the numerator and denominator into series of the form

$$1 + 2x + 3x^2 + \ldots = \frac{1}{(1-x)^2} \tag{10.5.8}$$

and

$$1 + x + x^2 + \ldots = \frac{1}{1-x} \tag{10.5.9}$$

where

$$x = e^{-\beta h\nu}$$

we find that

$$\bar{\epsilon} = \frac{1}{2} h\nu + h\nu \frac{e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} \tag{10.5.10}$$

$$E = 3N\bar{\epsilon}$$

$$= 3N \left( \frac{1}{2} h\nu + h\nu \frac{e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} \right) \tag{10.5.11}$$

and

$$\left( \frac{\partial E}{\partial T} \right)_v = C_v$$

$$= 3Nk \left( \frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \tag{10.5.12}$$

or

$$C_v = 3R \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2}$$

where

$$\theta = \frac{h\nu}{k}$$

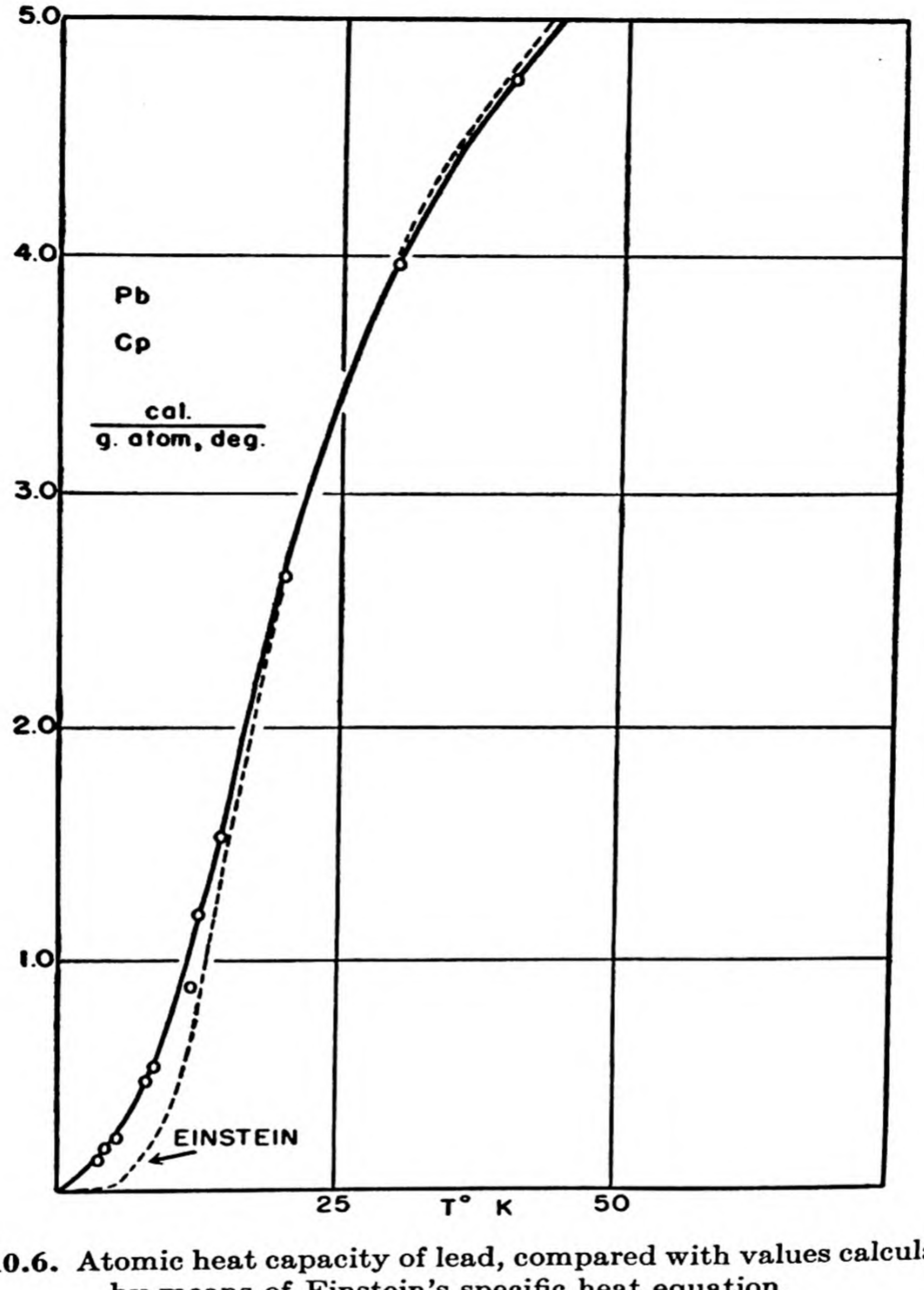



**Fig. 10.6.** Atomic heat capacity of lead, compared with values calculated by means of Einstein's specific heat equation.

Equation (10.5.12) describes qualitatively the decrease of $C_v$ with temperature, and gives a zero value of $C_v$ at the absolute zero in accordance with expectations from the third law of thermodynamics. Since each element will have its own fundamental frequency of vibration, its own $\theta$ value, Eq. (10.5.12) allows for the observed fact that different metals have quite different heat capacity values

at temperatures below the point where the law of Dulong and Petit is valid. It is also possible to show that as $T$ increases $C_v$ approaches the value $3R$.

Quantitative agreement between Eq. (10.5.12) and observation is very good, except in the neighborhood of the absolute zero as illustrated in Fig. 10.6. The latter is disappointing, because knowledge of the variation of heat capacity as the temperature is lowered to the absolute zero is most desirable in order to test the third law of thermodynamics. Equation (10.5.12) gives too low values, because it neglects the existence of low frequencies. It will be remembered that in the derivation of (10.5.12) the assumption was made that all the atoms in the crystal have only one and the same fundamental frequency $\nu$. It was assumed that the atoms act as independent oscillators without any good evidence that this is true. In fact at low temperatures we might expect that the independence of oscillation was not true, that the solid might act as an elastic solid in which standing waves could be established. This is the point of view adopted by Debye, whose theory of specific heats of solids we shall now describe.

## 10-6. *Debye's theory of the specific heat of solids*

The chief problem in any attempt to construct the partition function for crystalline solids is to enumerate the frequencies of the normal modes of vibration of the crystal. When this has been done, the heat capacity can then be calculated, either analytically, or if necessary, by graphical evaluation of the relevant integrals. Debye made his enumeration by assuming that standing waves were established in the crystal such that the half wavelength $\frac{1}{2}\lambda$ for a wave parallel to the $x$ axis, let us say, when multiplied by any integral number, be equal to the length of the crystal in the $x$ direction or

$$n(\tfrac{1}{2}\lambda) = a \tag{10.6.1}$$

where $a$ is the length of the box in the $x$ direction and $n$ is any integral number. Physically, this means that the nodes must coincide with the boundaries of the crystal. The longest wavelength would be the value of $\lambda$ when $n$ is equal to unity. This would give the lower limit to the frequency; a limit that according to (10.6.1) would depend on the dimensions of the box. However, as the fraction

of the energy involved in the waves of such long wavelength is negligible, we need not consider the shape of the crystal. The lower limit to the half wavelength will presumably be of the order of magnitude of the distance between atoms in the crystal; this sets an upper limit to the possible frequencies.

The velocity of propagation of the elastic waves in the solid is about ten times the velocity of sound waves in air. As the frequency multiplied by the wavelength is equal to the velocity, we can obtain an estimate of the highest possible frequency $\nu_m$ by dividing the velocity, $3 \times 10^{-5}$ cm./sec., by twice the distance between atoms in the crystal, 7 Å for lead, for example, or

$$\nu_m = \frac{3 \times 10^5}{7 \times 10^{-8}} = 4 \times 10^{12}$$

This is the frequency of infrared (far infrared) vibrations of light waves. In Debye's theory of specific heats it is assumed that the velocity of propagation of the elastic waves is independent of the wavelength.

We have to consider three types of waves in the elastic solid, one whose vibrations are longitudinal like sound waves in a fluid, and two with transverse vibrations, all three being propagated in the same direction. There are three independent directions of propagation. The velocities of propagation of the three types depend on the elastic constants of the solid and are the same for the two transverse waves. In an isotropic crystal the velocities will be independent of direction. We have now to determine the total number of the normal modes of vibration. Let us consider first a one-dimensional case, such as standing waves set up in a vibrating string of length $a$. Let $i$ be the total number of all possible modes whose longest wavelength is equal to $2a$ and whose shortest wavelength is limited, as mentioned above, by the internuclear distances. Let $\lambda_m$ be the shortest wavelength of the waves established in the solid, or in our one-dimensional example, in the string. Then

$$i = \frac{a}{\lambda_m/2} = \frac{2a}{\lambda_m} \tag{10.6.2}$$

In Fig. 10.7, we illustrate Eq. (10.6.2) with an example of standing waves such that $\lambda_m$ is equal to $\frac{1}{2}a$. Inserting this value of $\lambda_m$ into (10.6.2), we obtain 4 as the number of possible modes. This agrees

with the number drawn in Fig. 10.7, where we have waves for

$$\lambda = 2a, \quad \lambda = a, \quad \lambda = \tfrac{2}{3}a, \quad \lambda = \tfrac{1}{2}a$$

or $\frac{1}{2}\lambda$ equals 1, $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}a$.

Figure 10.8 represents the expansion of our example of standing waves in a crystal to the two-dimensional case. Note that both sides

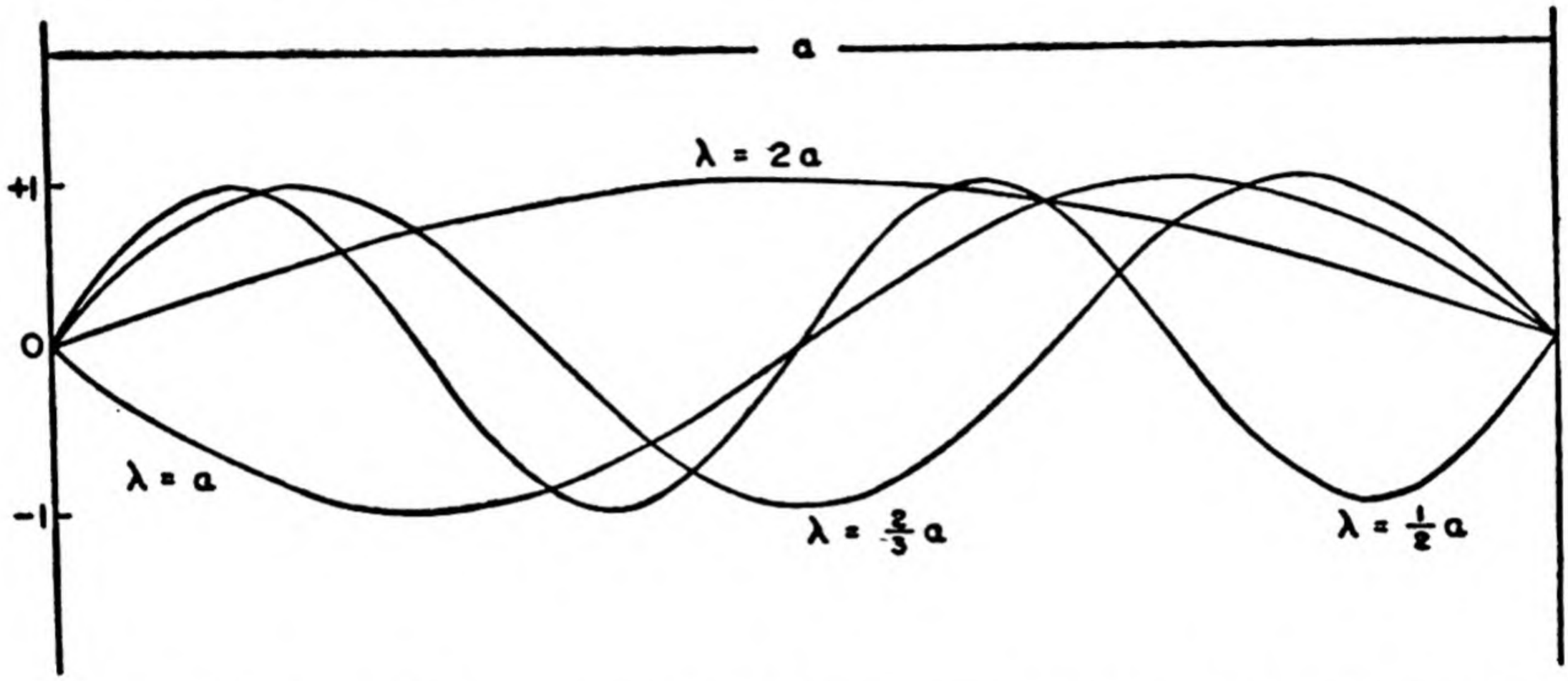



**Fig. 10.7.** Standing waves of different wavelengths. To avoid confusion, only half of each standing wave is shown.

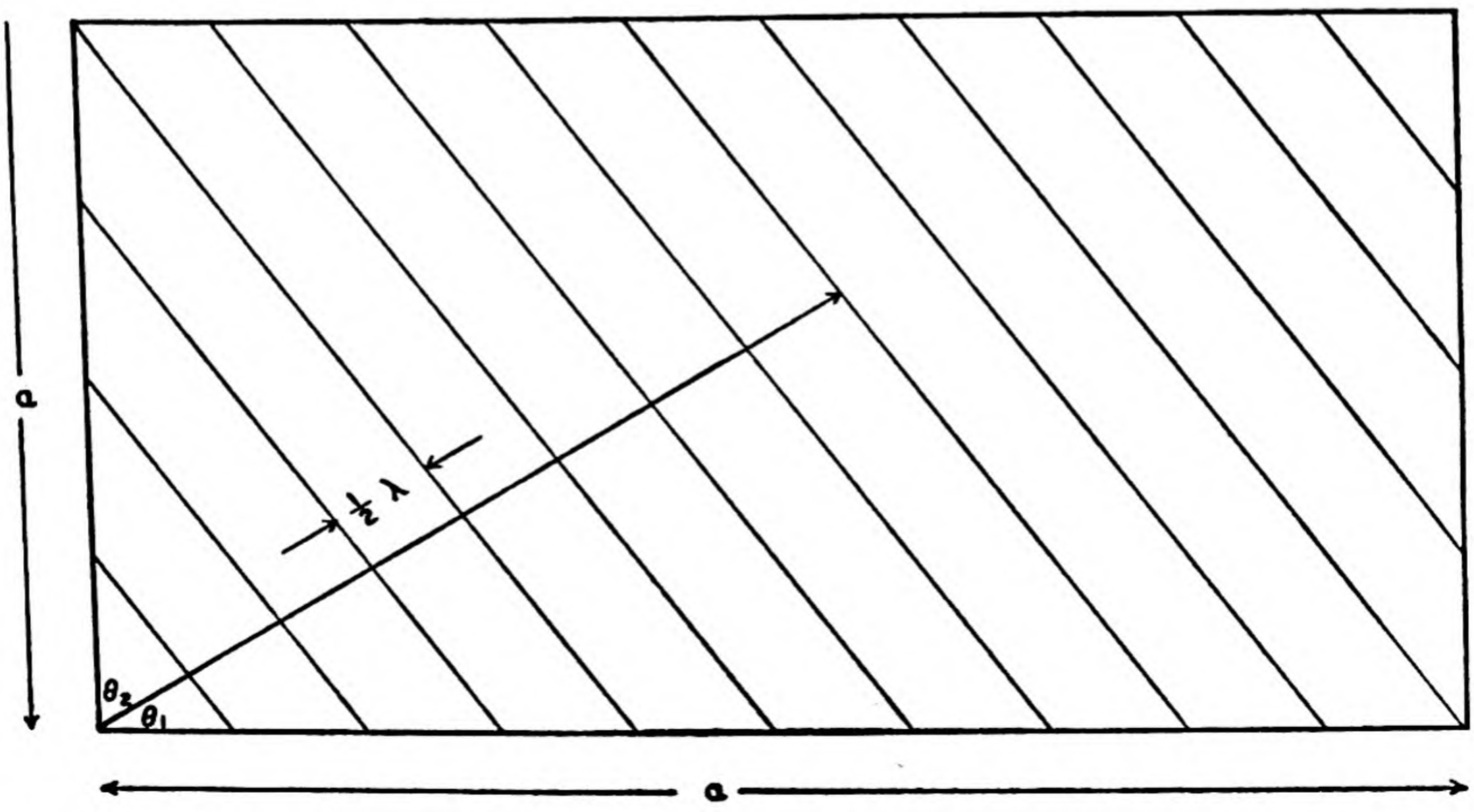



**Fig. 10.8.** The nodes of standing waves in a two-dimensional crystal.

of the frame are divided into an integral number of waves. The number of half waves or nodes that the horizontal side $a$ is divided into is given by the length $a$ divided by the projection of $\frac{1}{2}\lambda$ onto this length. The projection is equal to $\frac{1}{2}\lambda/\cos\theta_1$; hence the number of nodes along the horizontal axis is

$$i_x = \frac{a}{\frac{1}{2}\lambda_m/\cos\theta_1} = \frac{2a\cos\theta_1}{\lambda_m}$$

Similarly, the number of nodes along the vertical axis is

$$i_y = \frac{2a\cos\theta_2}{\lambda_m}$$

If a third dimension is considered, we would have

$$i_z = \frac{2a\cos\theta_3}{\lambda_m}$$

Now by geometry,

$$\begin{aligned} i_x^2 + i_y^2 + i_z^2 &= \frac{4a^2}{\lambda_m^2}(\cos^2\theta_1 + \cos^2\theta_2 + \cos^2\theta_3) \\ &= \frac{4a^2}{\lambda_m^2} \end{aligned} \tag{10.6.3}$$

Equation (10.6.3) represents the general restriction on the wavelengths that can be established in a cubical box or crystal.

Equation (10.6.3) is the equation for a sphere whose radius is $2a/\lambda_m$; we need to know all possible combinations of the positive integers, $i_x$, $i_y$, $i_z$ in order to know the total number of frequencies. This will be equal to the volume of the octant, or one-eighth of the sphere, since only in this octant of the sphere will all the integers, $i_x$, $i_y$, and $i_z$ be positive. Let $q_m$ be the total maximum number of possible modes; then

$$q_m = \frac{4}{3}\pi\frac{a^3}{\lambda_m^3} \tag{10.6.4}$$

Equation (10.6.4) refers to the number of modes of one type of wave, replacing $1/\lambda_m$ by $\nu_m/c$, and remembering that two transverse and one longitudinal wave must be counted for each direction of propagation, $q_m$ becomes

$$q_m = \frac{4}{3}\pi a^3\nu_m^3\left(\frac{2}{c_t^3} + \frac{1}{c_l^3}\right) \tag{10.6.5}$$

Equation (10.6.5) gives us the total number of modes when $\nu$ is equal to $\nu_m$; if $\nu$ is less than $\lambda_m$,

$$q = \frac{4}{3}\pi a^3 \nu^3 \left(\frac{2}{c_t{}^3} + \frac{1}{c_l{}^3}\right) \tag{10.6.6}$$

The total number of modes, $q_m$, must be equal to the total number of degrees of freedom $3N$, where $N$ is the number of atoms in one gram atomic weight of the crystal (Avogadro's number). Hence

$$q_m = 3N$$

and

$$\frac{4}{3}\pi a^3 \left(\frac{2}{c_t{}^3} + \frac{1}{c_l{}^3}\right) = \frac{3N}{\nu_m{}^3}$$

or

$$dq = \frac{9N}{\nu_m{}^3} \nu^2 \, d\nu \tag{10.6.7}$$

Equation (10.6.7) gives us the number of independent waves with frequencies between $\nu$ and $\nu + d\nu$.

We can regard each of these modes as a harmonic oscillator whose average energy we have already found in the previous section, Eq. (10.5.10). The total vibrational energy of the crystal in the range of frequencies between $\nu$ and $\nu + d\nu$ is therefore

$$dE = \bar{\epsilon} \frac{9N}{\nu_m{}^3} \nu^2 \, d\nu \tag{10.6.8}$$

or introducing the average value of the energy (omitting the zero point energy, which does not affect the specific heat),

$$E = 9 \frac{N}{\nu_m{}^3} \int_0^{\nu_m} \frac{h\nu^3}{e^{h\nu/kT} - 1} \, d\nu \tag{10.6.9}$$

Before integrating (10.6.9) it is convenient to introduce the variable $x$ and the constant $\theta$ (called the Debye temperature).

$$x = \frac{h\nu}{kT} \tag{10.6.10}$$

$$\theta = h\nu_m/k \tag{10.6.11}$$

Making these substitutions, Eq. (10.6.9) becomes

$$E = 9RT \left(\frac{T^3}{\theta^3}\right) \int_0^{x_m} \frac{x^3}{e^x - 1} \, dx \tag{10.6.12}$$

The integral in Eq. (10.6.12) is sometimes known as Debye's integral; it cannot be integrated explicitly except under conditions of high or low temperatures (where reasonable approximations can be made). Let us consider high temperatures where $x$ is very small and

$$e^x - 1 = 1 + x + \frac{x^2}{2} + \ldots - 1 \sim x$$

We have then, the simple integration

$$\int_0^x x^2\,dx = \frac{1}{3}x^3 = \frac{1}{3}\frac{\theta^3}{T^3}$$

and $$E = 3RT, \quad \text{and} \quad C_v = 3R$$

the law of Dulong and Petit.

At low temperatures we write the Debye integral in the form

$$\int_0^{x_m} \frac{x^3}{e^x - 1}\,dx = \int_0^{\infty} \frac{x^3}{e^x - 1}\,dx - \int_{x_m}^{\infty} \frac{x^3}{e^x - 1}\,dx \quad (10.6.13)$$

Now when $x_m$ becomes very large, as $T$ approaches zero, the integrand

$$\frac{x^3}{e^x - 1}$$

approaches zero, and the second integral on the right side of Eq. (10.6.13) can be neglected. The value of the definite integral

$$\int_0^{\infty} \frac{x^3}{e^x - 1}\,dx$$

is known and is equal simply to $\pi^4/15$; hence at low temperatures, the equation for the vibrational energy of the crystal becomes

$$E = 9RT\left(\frac{T^3}{\theta^3}\right)\frac{\pi^4}{15} \quad (10.6.14)$$

and

$$C_v = \frac{36}{15}\pi^4 R\,\frac{T^3}{\theta^3} \quad (10.6.15)$$

Equation (10.6.15) is known as Debye's "$T$-cubed law," and has proved invaluable in extrapolation of the heat capacities of crystals from temperatures in the liquid hydrogen range (20°K) to the absolute zero. It tells us that the heat capacity should vary as the third power of the temperature, and that the heat capacity should

be zero at the absolute zero of temperature. This relationship between $T^3$ and $C_v$ has been amply verified, not only for monatomic crystals, but also for many crystalline compounds, as illustrated in Fig. 10.9.

This treatment of the specific heat of solids has been given in the simplest possible form, it neglects uncertainties in the frequencies

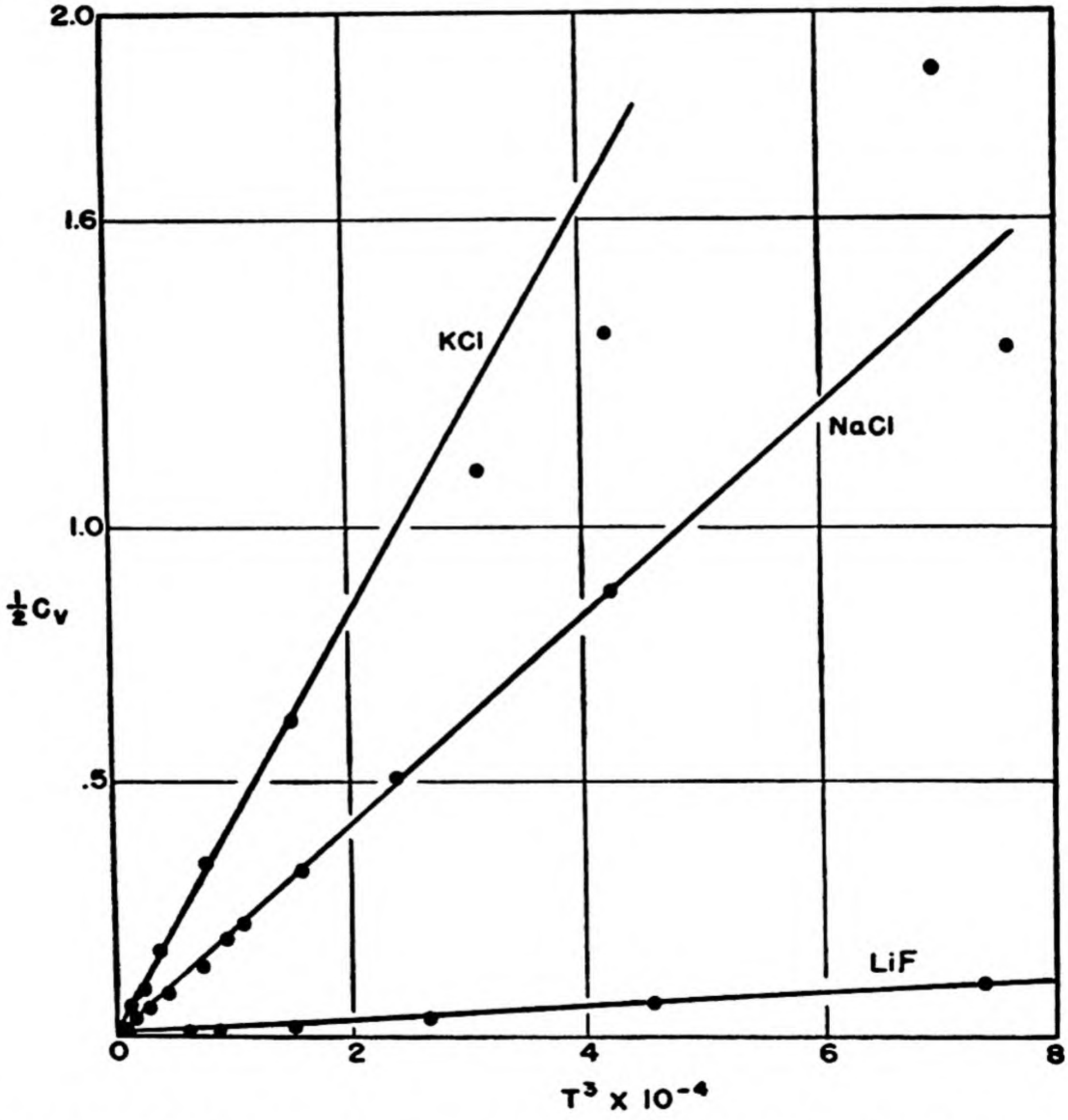



**Fig. 10.9.** Half molal heat capacities of KCl, NaCl, and LiF crystalline solids, illustrating agreement with the Debye $T^3$ law.

of the waves when the wavelength approaches molecular dimensions, the possible electronic contributions to the specific heat, the vibrations of constant $\nu$ within molecules, sometimes called "the Einstein terms," the transition of vibration to rotation as the temperature is raised such as occurs with HCl, $CH_4$, and other mole-

cules, and unusual deviations at very low temperatures from the predicted behavior. We take up in the next section some interesting aspects of the specific heat at low temperatures.

## 10-7. *Some special aspects of the specific heats of solids at low temperature*

It is possible to develop theoretical specific heat equations along the lines of the Debye theory for two-dimensional and one-dimensional crystals, as was apparently done for the first time by Tarasov.[8] Examples of such crystals are graphite and boron nitride, whose atoms form hexagonal rings that are combined together in sheets of hexagons with small binding energy between the sheets. Forces between atoms in the plane of the sheets are strong, but are weak in a direction transverse to the sheet; hence at very low temperatures we can consider that vibrational displacements occur only perpendicularly to the plane of the sheets. We have then to count only the frequencies of vibration of the waves whose vibrations are perpendicular to the plane of the sheet. The waves in a two-dimensional crystal are represented by Fig. 10.8. The result of such an enumeration of the frequencies is at very low temperatures

$$C_v = 14.4 \frac{RT^2}{\theta^2} \tag{10.7.1}$$

where the straightforward calculation has been divided by 3 because only waves with perpendicular displacements are to be considered. For molecules containing two atoms, the constant of Eq. (10.7.1) should be multiplied by 2. Note that Eq. (10.7.1) predicts that the heat capacity will vary with $T$-squared rather than $T$-cubed, and is in excellent agreement with the data[9] as far as the variation of $C_v$ with $T$ is concerned (see Fig. 10.10).

[8] V. V. Tarasov, *Compt. rend. acad. sci. U. R. S. S.*, Vol. 46, No. 3, 1945; *ibid.*, Vol. 54, No. 9, 1946; *Zhur. Fiz. Khim.*, **1,** 111 (1950). Tarasov's papers have been quoted by W. DeSorbo, *J. Chem. Phys.*, **21,** 168, 764 (1953), and by J. T. Law, *J. Chem. Phys.*, **20,** 1329 (1952). Apparently unaware of Tarasov's work, R. W. Gurney also has discussed two-dimensional crystals in *Phys. Rev.*, **88,** 465 (1952).

[9] Data for Fig. 10.9 were taken from the paper of Gurney, who quotes unpublished results of Estermann and Kirkland on graphite [see W. DeSorbo and W. W. Tyler, *Phys. Rev.*, **83,** 878 (1951) for a recent study of the heat capacity of graphite], and from work of A. S. Dworkin, D. J. Sasmor, and E. R. VanArtsdalen, *J. Chem. Phys.*, **21,** 954 (1953) on boron nitride.

Let us now consider the validity of the Debye theory of specific heats, which seems to be amply verified as far as the $T$-cubed law is concerned by the data illustrated in Fig. 10.9. As a matter of fact, if the Debye temperature, the $\theta$ constant of Eq. (10.6.12), is calcu-

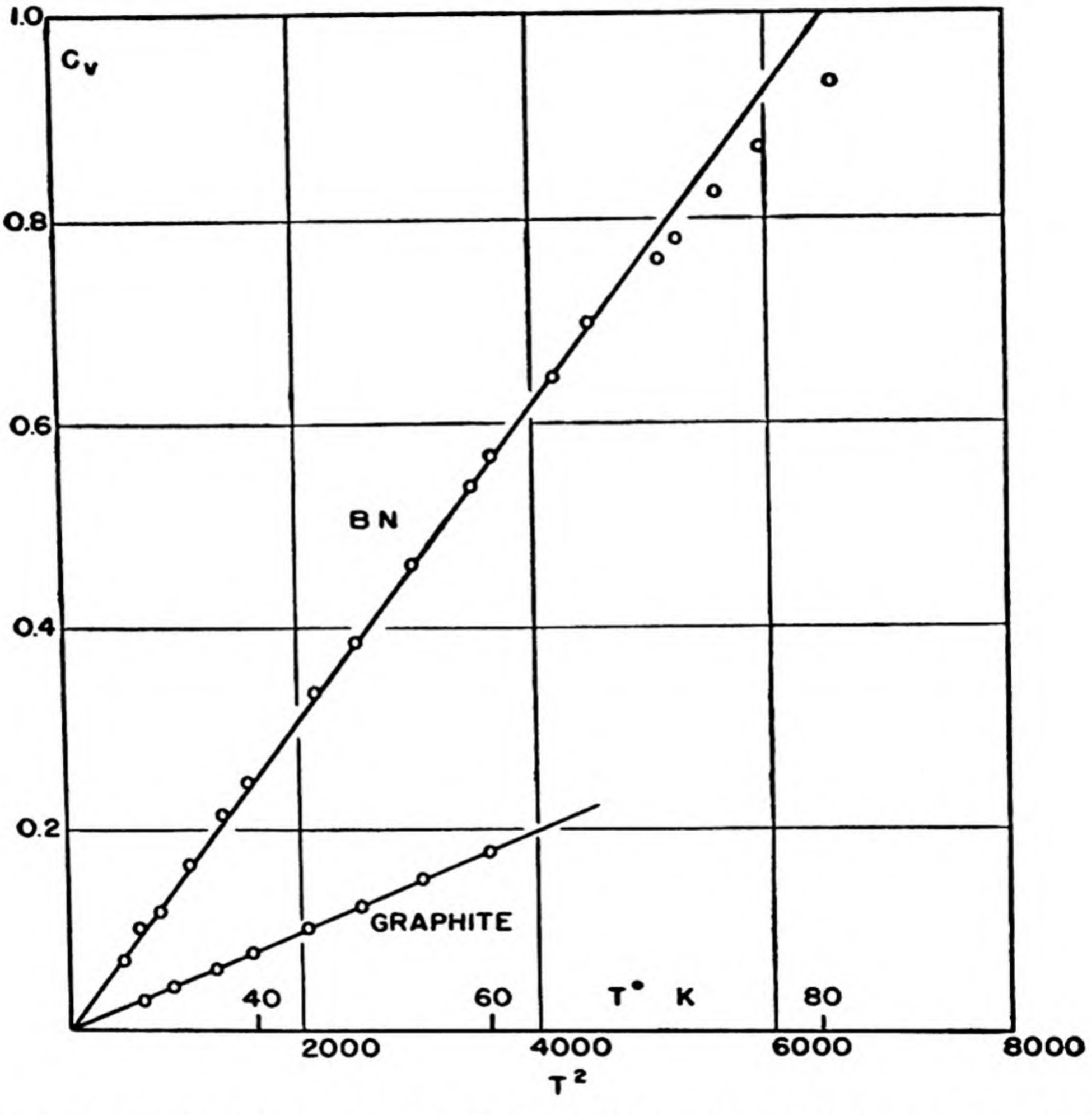



**Fig. 10.10.** Molal heat capacities of BN and atomic heat capacity of graphite in the solid state, illustrating the $T^2$ heat capacity law.

lated over a wide temperature range, it is not found to be constant as it should be if the theory is valid. Some recently published values of $\theta$ for the crystalline alkali halides of Fig. 10.9 taken from a paper of Clusius, Goldmann, and Perlick[10] are shown in Fig. 10.11, where a wide variation of $\theta$ with temperature is evident, particularly for

[10] K. Clusius, J. Goldmann, and A. Perlick, *Z. Naturforsch*, **4A**, 424 (1949).

LiF. These changes of $\theta$ with $T$ are not large enough to invalidate the use of the Debye $T$-cubed law in calculating absolute entropies (see Chap. 12); nevertheless, from a theoretical standpoint it is interesting to inquire into the physical reason for the variation of $\theta$ with $T$. Let us consider sodium chloride.

If the atomic structure of the crystal is examined and an exact calculation is made of the possible frequencies that can be propa-

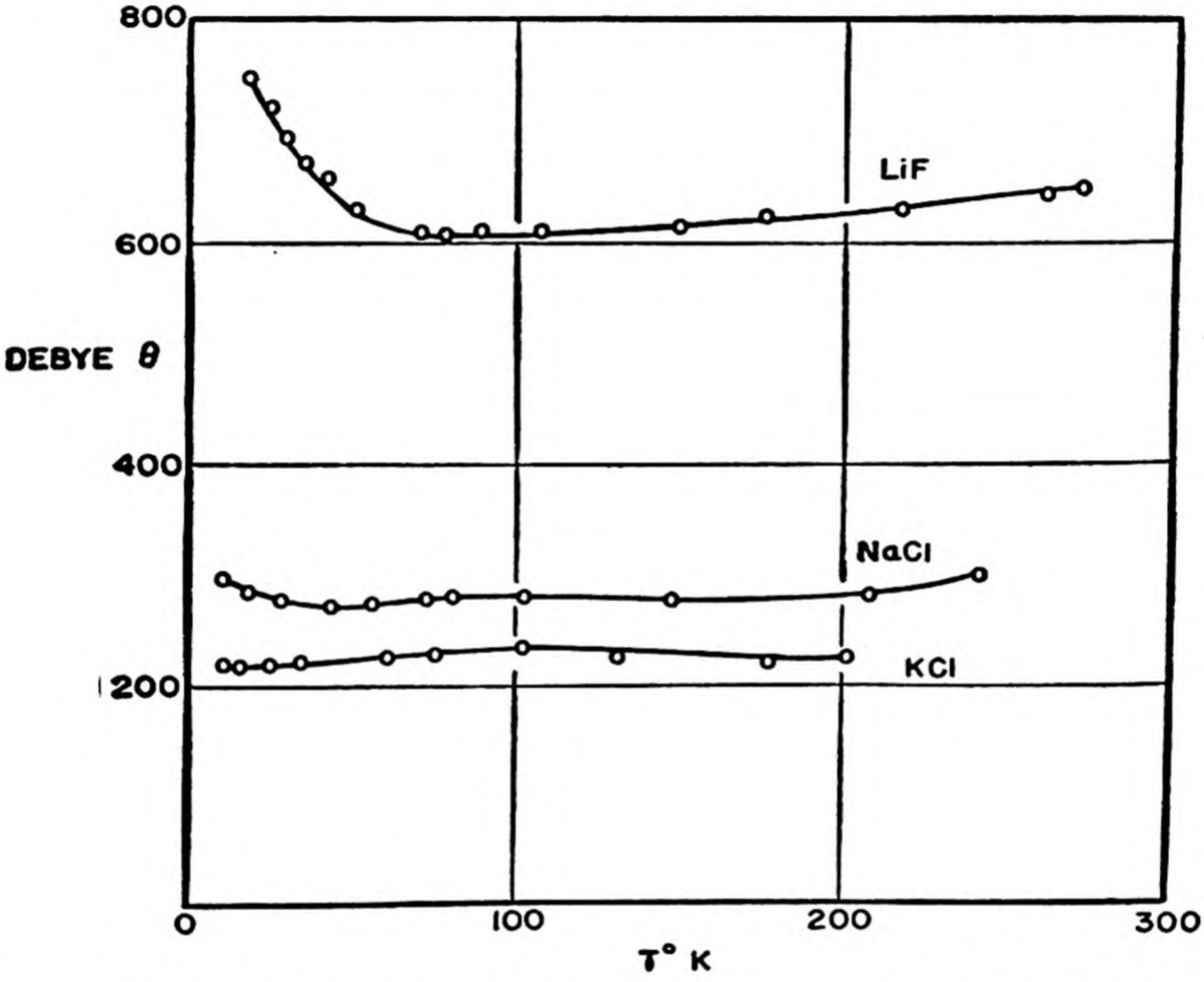



**Fig. 10.11.** Variation of the Debye $\theta$ with temperature, for KCl, NaCl, and LiF.

gated in the crystal, the fraction of modes whose frequencies lie between $\nu$ and $\nu + d\nu$ is found not to be exactly proportional to $\nu^2$ as assumed in the Debye theory. This fact is illustrated in Fig. 10.12, where it can be seen that at low frequencies there is excellent correspondence between the calculated curve for NaCl and the Debye theory curve, but at high frequencies considerable deviations occur. At high frequencies the wavelengths are short and the possible frequencies are determined by the atomic structure of the crystal;

at low frequencies the wavelengths are long, and treatment of the crystal as an isotropic elastic continuum is satisfactory. The frequencies of the NaCl crystal illustrated in Fig. 10.12 were calculated by Kellerman,[11] using the Born model of the ionic lattice. The maximum in the frequency distribution curve occurs at a frequency

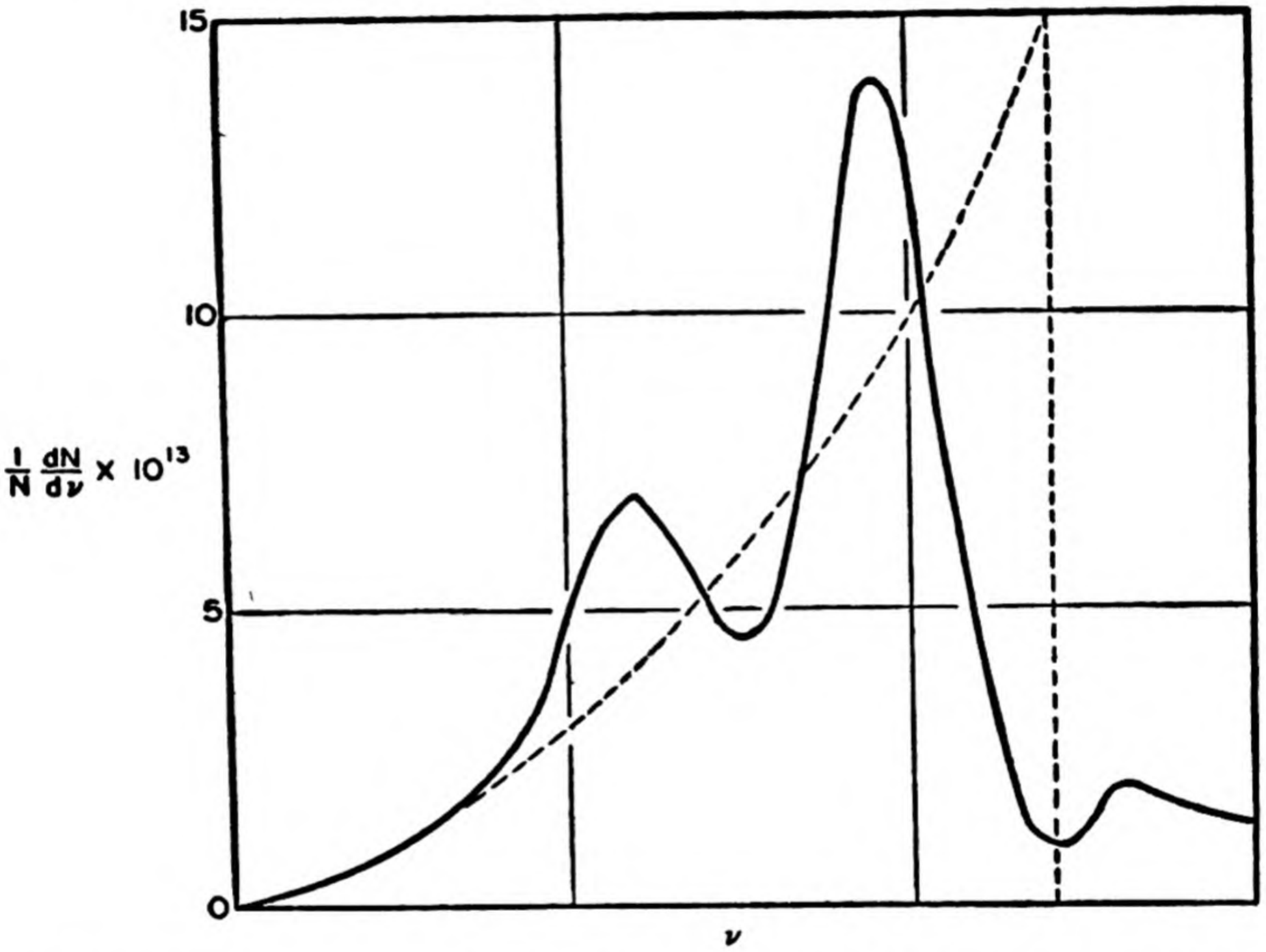



**Fig. 10.12.** Frequency distribution of the standing waves in crystalline NaCl. Solid line calculated from the Born model; dashed line, the $\nu^2$ function used by Debye.

whose intensity is strong in the infrared absorption spectrum of NaCl.

If the frequency distribution calculated by Kellerman is used in the Debye theory, the Debye $\theta$ values agree within the experimental uncertainties with the values shown in Fig. 10.11. Thus it can be concluded that if the frequency distribution such as illustrated in Fig. 10.12 is known for any crystal, its specific heat can be accurately calculated. Unfortunately, calculation of the frequency distribution

[11] E. W. Kellerman, *Philos. Trans. Roy. Soc.*, London, **238A**, 513 (1940); *Proc. Roy. Soc.*, London, **178A**, 17 (1941).

is very involved and difficult and has been carried out only for a very few crystals.

Jura and Pitzer[12] have discussed the effect of particle size on the heat capacity of crystals in the neighborhood of the absolute zero. Their calculations indicate that at 1°K the gross translation and rotation of whole particles constitute the principal contributions to the heat capacity in the case of cubes of aluminum 100 Å on edge; the heat capacity of the small crystal will be greater than that of the infinitely large crystal.

Silvidi and Daunt[13] could detect no contribution to the specific heat resulting from the small sizes of Zn down to particle sizes of $10^{-4}$ cm. At 1.5°K the contribution to the specific heat due to elastic vibrations in the solid, Debye terms, amounted to only 20% of the total, inasmuch as the electronic contribution was relatively large at this temperature. Thus Silvidi and Daunt found that for tungsten and zinc at very low temperatures the gram atomic heat capacity obeyed the equation

$$C_v = AT + BT^3 \qquad (10.7.2)$$

where the term in $T$ represents the electronic contribution. To understand the behavior of electrons in the metals it is necessary first to become acquainted with the Fermi-Dirac distribution law and statistics. This subject is taken up briefly in Chapter 14.

The heat capacity of solid hydrogen may increase with decrease of temperature near the absolute zero, because of complications resulting from the presence of *ortho*-hydrogen. Figure 10.13 illustrates data obtained by Mendelssohn, Ruhemann, and Simon[14] on three samples of solid hydrogen containing 99.2, 50, and 25 per cent *para*-hydrogen, respectively. In the 99.2% *para*-hydrogen there are no specific heat anomalies because of the almost complete absence of *ortho*-hydrogen, but in the *ortho-para* mixtures the change in the population of the three $(2j + 1)$ lowest rotational states of *ortho*-hydrogen $(j = 1)$ causes increased absorption of energy with increase of temperature as the temperature of the sample is lowered below 6°K. This is because the energy difference between these

[12] G. Jura and K. S. Pitzer, *J. Am. Chem. Soc.*, **74**, 6030 (1952); see also E. W. Montroll, *J. Chem. Phys.*, **18**, 183 (1950).

[13] A. A. Silvidi and J. G. Daunt, *Phys. Rev.*, **77**, 125 (1950).

[14] K. Mendelssohn, M. Ruhemann, and F. Simon, *Z. physik. Chem.*, **15B**, 121 (1932).

states, which are considered degenerate above 11°K, is of the order of magnitude of $kT$ at these very low temperatures.

Another example of a heat capacity of a solid increasing with decrease of temperature near the absolute zero is given by the magnetic studies of Roberts, Sartain, and Borie[15] on neodymium

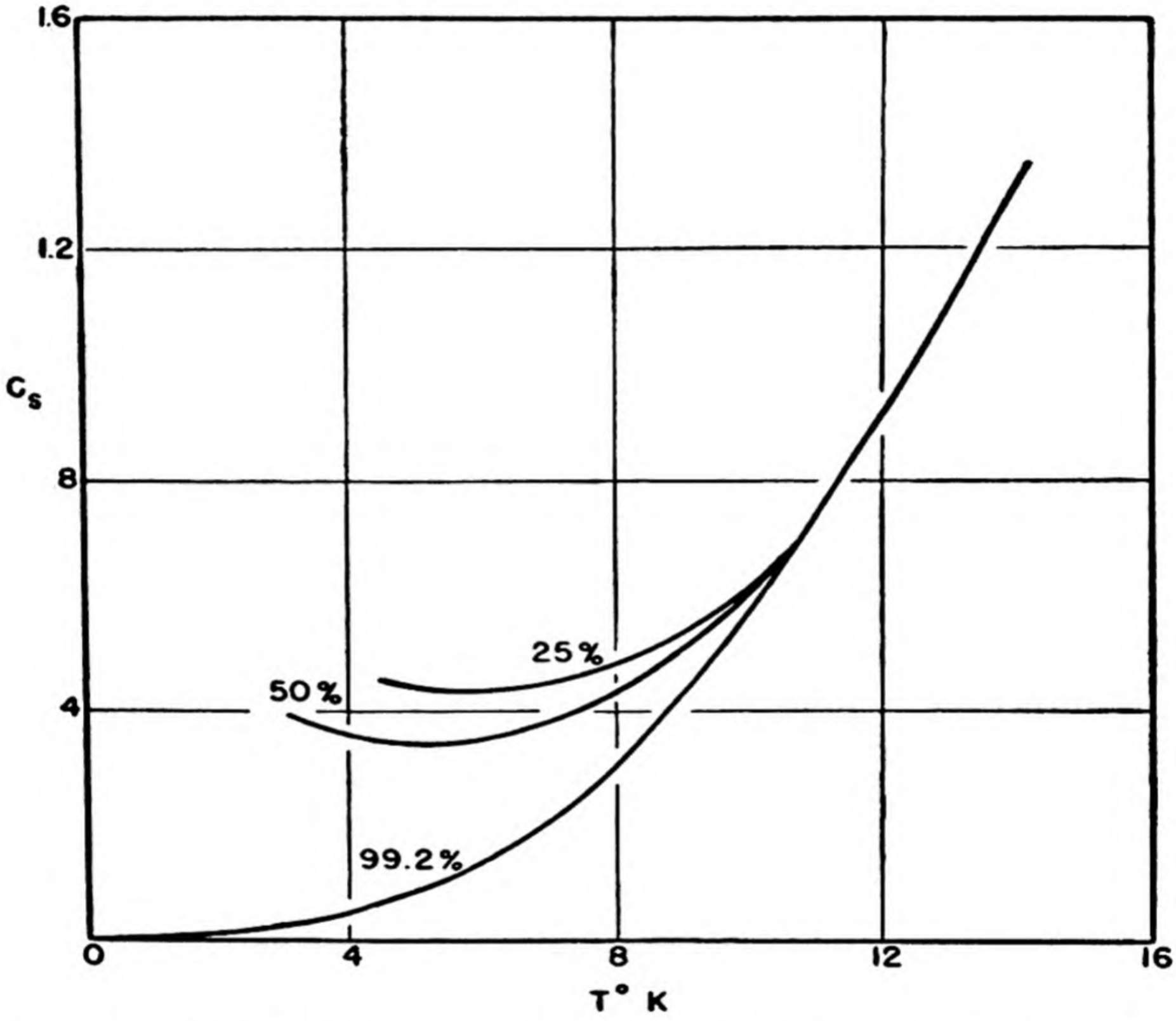



**Fig. 10.13.** Molal heat capacity of solid hydrogen at its saturated vapor pressures. The percentages on the curves indicate the percentage of *para*-hydrogen.

ethylsulfate, $Nd(C_2H_5SO_4)_3 9H_2O$ over the temperature range 0.95 to 2.15°K. Excluding the contribution to the specific heat due to elastic vibrations in the solid (lattice effects), the heat capacity at constant magnetization $C_I$ can be expressed by

$$C_I = \frac{b}{T^2}$$

where $b$ is composed of two terms, $b_e$ and $b_n$, the first produced by electron dipole-dipole interaction, and the second by electron

[15] L. D. Roberts, C. C. Sartain, and B. Borie, *Revs. Modern Phys.*, **25**, 170 (1953).

nuclear interaction (hyperfine coupling). The measurements of $C_I$ were carried out by a magnetic method whose description is beyond the scope of this book. In order to separate the constant $b$ into its component terms $b_e$ and $b_n$, Roberts, Sartain, and Borie, in addition to using normal neodymium, made use of two samples of neodymium whose isotopic composition had been altered in the giant electro-

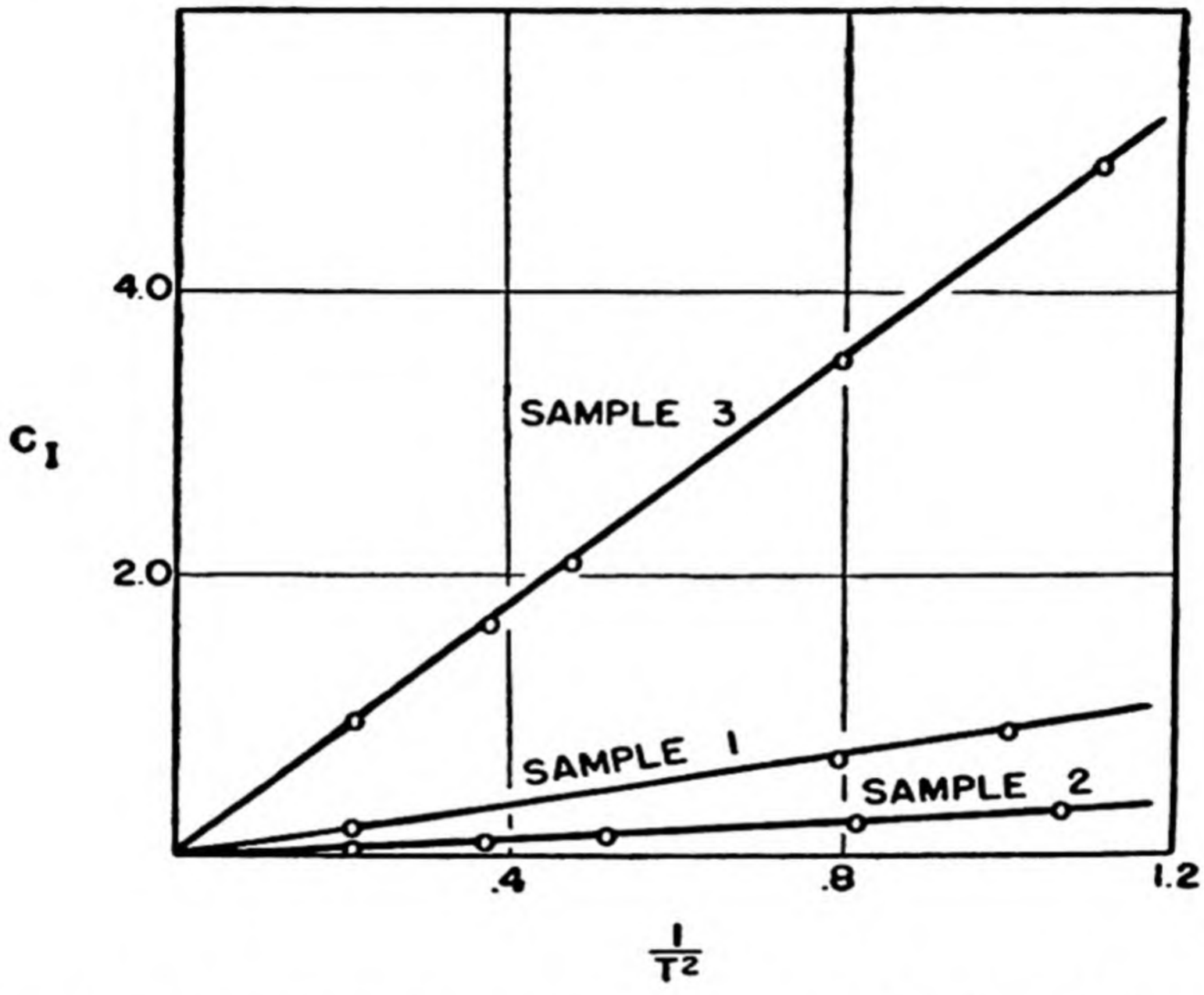



**Fig. 10.14.** Heat capacity at constant magnetization of three samples of neodymium ethylsulfate of different neodymium isotope abundance. The lattice vibration contribution to the heat capacity has been eliminated from the measured values.

magnetic isotope-separating machines at Oak Ridge. The isotopic composition of the three samples was as given in Table 10.2.

TABLE 10.2

| *Isotope mass* | ISOTOPE ABUNDANCE OF NEODYMIUM | | |
|---|---|---|---|
| | *Sample 1 (normal)* | *Sample 2* | *Sample 3* |
| 142 | 27.13 | 93.00 | 4.04 |
| 143 | 12.20 | 3.18 | 83.93 |
| 144 | 23.87 | 2.89 | 8.83 |
| 145 | 8.30 | 0.368 | 1.78 |
| 146 | 17.18 | 0.414 | 1.16 |
| 148 | 5.72 | 0.084 | 0.149 |
| 150 | 5.60 | 0.066 | 0.108 |

The reason for studying samples of different isotopic composition was that $b_e$ is independent of isotopic composition, but that $b_n$, being the term arising from nuclear spin-electron spin interactions, does depend on the constitution of the nucleus. Data for $C_I$ obtained by Roberts, Sartain, and Borie are illustrated in Fig. 10.14. From the equations for these lines, the authors obtained the following values of the constants.

$$b_e = 0.146 \times 10^5 \text{ erg deg.}$$
$$b_n \text{ (isotope 143)} = 5.08 \times 10^5 \text{ erg deg.}$$
$$b_n \text{ (isotope 145)} = 1.7 \times 10^5 \text{ erg deg.}$$

## PROBLEMS

**1.** Derive the equation for the electronic contribution to the heat capacity for a gas whose electronic partition function is

$$Q_{elec.} = g_0 + g_1 e^{-\beta\epsilon_1}$$

**2.** Which of the following substances might be expected to have *ortho-para* forms, what would be the high-temperature ratio of *ortho* to *para*, and which form would be the stable one at 0°K?

(a) $Li^6Li^6$; (b) $Li^6Li^7$; (c) $Li^7Li^7$; (d) $Li^7H^1$.

**3.** To how low a temperature would $Li^7Li^7$ have to be cooled (assuming it to exist as a perfect gas for the purposes of this problem) before a change in the *ortho-para* ratio could be significantly detectable? Make your estimate by a comparison with $H_2$ or $D_2$, or, better still, calculate $C_{rot.}$ as a function of temperature, and from a plot estimate the temperature at which $C_{rot.}$ becomes equal to the classical value.

**4.** Compute the molal heat capacity $C_p$ of methane at 873°K and compare with the experimentally observed value of 16.8 calories per degree per mole.

**5.** Prove that according to Eq. (10.5.12) $C_v$ goes to zero at the absolute zero of temperature.

**6.** Derive the low-temperature theoretical specific heat equation for a two-dimensional solid, Eq. (10.7.1). *Hint:* The total number of degrees of freedom in this case is $3N$. The definite integral

$$\int_0^\infty \frac{x^2}{e^x - 1}\, dx$$

has the value 2.40.

**7.** Derive the low-temperature specific heat equation for a one-dimensional crystal such as a fiber. Assume that vibrational displacements may occur normal to the fiber axis but not in the direction of the fiber chain. Take the total degrees of freedom to be $3N$. *Hint:* The definite integral

$$\int_0^\infty \frac{x}{e^x - 1}\, dx$$

has the value $\pi^2/6$.

# *Chapter 11*

# CALCULATION OF EQUILIBRIUM CONSTANTS IN TERMS OF PARTITION FUNCTIONS

11-1. Thermodynamic Relations between Free Energy, Equilibrium Constants, and Partition Functions. 11-2. Calculation of Isotopic Exchange Equilibrium Constants. 11-3. The Problem of Internal Rotation. 11-4. Detailed Calculation of a Chemical Equilibrium Constant.

## 11-1. *Thermodynamic relations between free energy, equilibrium constants, and partition functions*

Inasmuch as the free energy change in a reaction for all the reactants and the products in their standard states (for gases, 1 atmosphere pressure), $\Delta F^\circ$, is related to the equilibrium constant by the equation

$$\Delta F^\circ = -RT \ln K_p \tag{11.1.1}$$

and inasmuch as we can express the molal free energy of gases in their standard states in terms of the partition function by the equation

$$F^\circ = -RT \ln \frac{Q^\circ}{N} \tag{11.1.2}$$

it is clear that the equilibrium constant can be directly expressed in terms of the partition function for gases in their standard states. Consider the general equilibrium between gases

$$a\mathrm{A} + b\mathrm{B} \rightleftarrows c\mathrm{C} + d\mathrm{D} \tag{11.1.3}$$

For this equilibrium, the equation for the equilibrium constant in terms of the partition function is

$$K_p = \frac{(Q^\circ_\mathrm{C}/N)^c (Q^\circ_\mathrm{D}/N)^d}{(Q^\circ_\mathrm{A}/N)^a (Q^\circ_\mathrm{B}/N)^b} \tag{11.1.4}$$

Sometimes the equilibrium is expressed by the equation

$$-R \ln K_p = \frac{\Delta F^\circ}{T} = \frac{\Delta E^\circ}{T} + c\frac{(F^\circ - E_0^\circ)_C}{T} + d\frac{(F^\circ - E_0^\circ)_D}{T} - a\frac{(F^\circ - E_0^\circ)_A}{T} - b\frac{(F^\circ - E_0^\circ)_B}{T} \qquad (11.1.5)$$

Wagman, Kilpatrick, Taylor, Pitzer, and Rossini[1] have made a systematic tabulation over wide temperature ranges of the function $(F^\circ - E_0^\circ)/T$ for a number of simple and important molecules, $O_2$, $H_2$, $H_2O$, C (both as graphite and diamond), CO, $CO_2$, and $CH_4$. They also give values of the functions

$$\frac{H^\circ - H_0^\circ}{T}, \qquad H^\circ - H_0^\circ, \qquad C_p^\circ$$

$$\frac{F^\circ - H_0^\circ}{T}, \qquad S^\circ$$

$H_f^\circ$ [the heat of formation from the elements in their standard states for $H_2O$ (gas), CO, $CO_2$, and $CH_4$]

$\Delta F_f^\circ$, $\Delta H^\circ$, $\Delta F^\circ$, $\log K_f$

$\log K$ [for some reactions involving $O_2$, $H_2$, $H_2O$, C (graphite), CO, $CO_2$, and $CH_4$]

If the above functions were known for all chemical species, the equilibrium constants of all reactions could be calculated. It is one of the goals of physical chemistry to extend and amplify the list of molecules whose thermodynamic functions are completely known.

To illustrate the use of the Bureau of Standards tables, let us consider in detail the calculation of the equilibrium constant for the following equilibrium when established at 1000°$K$.

$$C + H_2O \rightleftarrows CO + H_2$$

From the tables we take the following information (at 1000°K):

| | CO | $H_2$ | C | $H_2O$ |
|---|---|---|---|---|
| $\frac{F^\circ - E_0^\circ}{T}$ | −48.860 | −32.738 | −2.771 | −47.018 |
| $\frac{H^\circ - E_0^\circ}{T}$ | 7.2565 | 6.9658 | 3.0746 | 8.580 |
| $H_f^\circ$ | −26,768 | 0 | 0 | −59,239 |
| $H_{0(f)}^\circ$ | −27,201.9 | 0 | 0 | −57,104.3 |

[1] *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

The units are calories per mole per degree centigrade, or calories per mole as the case may be. To calculate the equilibrium constant, we need make use only of the first and last row of numbers in the above table. Thus

$$\Delta \frac{(F^\circ - E_0^\circ)}{T} = -48.860 - 32.738 + 2.771 + 47.018$$
$$= -31.809$$
$$\frac{\Delta E_0^\circ}{T} = -27.2019 + 57.1043 = 29.902$$

whence

$$-R \ln K = 29.902 - 31.809 = -1.907, \qquad \text{or} \qquad K = 2.593$$

To assist in the calculation of the above functions for molecules not listed in the tables, Wagman, Kilpatrick, Taylor, Pitzer, and Rossini[1] give the following equations:

*Thermodynamic functions for translation.*

$$\frac{H - H_0^\circ}{T} = C_p = 4.9680$$
$$= RT \frac{\partial \ln Q_{trans.}}{\partial T} - \frac{H_0^\circ}{T}$$
$$\frac{F^\circ - H_0^\circ}{T} = -6.8635 \log M + 7.2820 - 11.4391 \log T$$
$$S^\circ = 6.8635 \log M - 2.3141 + 11.4391 \log T$$

*Thermodynamic functions for rotation. Rigid linear molecules.*

$$\frac{H^\circ - H_0^\circ}{T} = C_{rot.}^\circ = 1.9872$$
$$\frac{F^\circ - H_0^\circ}{T} = -4.5757 \log \left( \frac{T \cdot 10^{39}}{\sigma} \right) + 2.7676 - 4.5757 \log T$$
$$S^\circ = 4.5757 \log \left( \frac{I \cdot 10^{39}}{\sigma} \right) - 0.7804 + 4.5757 \log T$$

*Nonlinear polyatomic molecules.*

$$H^\circ - H_0^\circ = C_{rot.}^\circ = 2.9808$$

$$\frac{F^\circ - H_0^\circ}{T} = -2.2878 \log (I_A I_B I_C \cdot 10^{117}) + 4.5757 \log \sigma + 3.0140 - 6.8635 \log T$$

$$S^\circ = 2.2878 \log (I_A I_B I_C \cdot 10^{117}) - 4.5757 \log \sigma - 0.0332 + 6.8635 \log T$$

In the equations above, the energy unit is calories per mole, $M$ is the molecular weight in ordinary atomic weight units, and $I$ the moment of inertia in units of cm.$^2$ g.

No general equations can be given for the vibrational contributions, since these depend on the number, degeneracy, and magnitude of the vibrational frequencies.

For chemical substances whose free energy functions are not tabulated it is necessary to calculate their partition functions, using the complete partition function equations. They may be summarized as follows:

*Monatomic gases.*

$$Q = \frac{(2\pi mkT)^{3/2}}{h^3} V Q_{elec.} \tag{11.1.6}$$

*Diatomic gases.*

$$Q = \frac{(2\pi mkT)^{3/2}}{h^3} V \frac{8\pi^2 IkT}{\sigma h^2} \cdot \frac{1}{1 - e^{-h\nu/kT}} \cdot Q_{elec.} Q_{energy\ zero} \tag{11.1.7}$$

*Polyatomic gases.*

$$Q = \frac{(2\pi mkT)^{3/2}}{h^3} V \frac{8\pi^2}{\sigma h^3} [I_A I_B I_C]^{1/2} (2\pi kT)^{3/2} \prod_s \frac{1}{1 - e^{-h\nu_s/kT}} Q_{elec.} Q_{energy\ zero} \tag{11.1.8}$$

These equations reduce to particularly simple ratios when applied to isotopic exchange equilibria, so we shall first apply them to a few examples of this type of a chemical phenomenon.

## 11-2. *Calculation of isotopic exchange equilibrium constants*

Consider the isotopic exchange equilibrium

$$2H_2O^{18} + CO_2^{16} \rightleftarrows 2H_2O^{16} + CO_2^{18} \qquad (11.2.1)$$

If the isotopic species of oxygen, of mass 16 and 18, were randomly distributed between carbon dioxide and water, the equilibrium constant of the above equilibrium (11.2.1) would be equal to unity. If the translational, rotational, and vibrational partition functions could all be expressed by the classical equations, again the equilibrium constant would be equal to unity.[2]

In terms of the partition function, the equilibrium constant for (11.2.1) can be expressed by

$$K = \frac{\left[\frac{Q^\circ_{H_2O^{16}}}{N}\right]^2 \left[\frac{Q^\circ_{CO_2^{18}}}{N}\right]}{\left[\frac{Q^\circ_{H_2O^{18}}}{N}\right]^2 \left[\frac{Q^\circ_{CO_2^{16}}}{N}\right]} \qquad (11.2.2)$$

The $N$'s all cancel, so that it becomes convenient to evaluate the ratios of $Q^\circ_{H_2O^{18}}/Q^\circ_{H_2O^{16}}$ and $Q^\circ_{CO_2^{18}}/Q^\circ_{CO_2^{16}}$ or in general $Q^\circ_2/Q^\circ_1$, where the subscript 2 refers to the molecule with the heavier isotope. With respect to the translational contributions, the ratio becomes

$$\left(\frac{M_2}{M_1}\right)^{3/2} \qquad (11.2.3)$$

where $M$ signifies the molecular weight. The rotational partition function ratio reduces to

$$\left(\frac{I_{A_2} I_{B_2} I_{C_2}}{I_{A_1} I_{B_1} I_{C_1}}\right)^{1/2} \frac{\sigma_1}{\sigma_2} \qquad (11.2.4)$$

In (11.2.1) the symmetry numbers happen to be the same for all molecular species and will cancel, but in other equilibria they may not, and in fact, they often become the principal terms in the equilibrium constant equation. The ratio for vibration is

[2] This statement assumes that the electronic partition function is unchanged by the substitution of $O^{18}$ for $O^{16}$ and that the partition function factor for the energy zero is likewise unaffected by the substitution of $O^{18}$ for $O^{16}$ (equivalent to assuming no zero point energy). The proof of the theorem mentioned above is given as a problem at the end of the chapter.

$$\prod_s \frac{1 - e^{-h\nu_{s,2}/kT}}{1 - e^{-h\nu_{s,1}/kT}} \tag{11.2.5}$$

and for energy zero partition function factor

$$e^{-\frac{1}{2}\sum_s (h\nu_{s,2} - h\nu_{s,1})/kT} \tag{11.2.6}$$

In (11.2.6) the $\chi$ term has been omitted because it is assumed that the electronic structure of the atoms and the shape of the potential energy curves for molecule formation are unchanged when the atomic mass but not the atomic number of the nucleus is changed.

Combining (11.2.3), (11.2.4), (11.2.5), and (11.2.6) we obtain

$$\frac{Q_2^\circ}{Q_1^\circ} = \left(\frac{M_2}{M_1}\right)^{3/2} \left(\frac{I_{A_2} I_{B_2} I_{C_2}}{I_{A_1} I_{B_1} I_{C_1}}\right)^{1/2} \frac{\sigma_1}{\sigma_2} \cdot e^{-\frac{1}{2}\sum_s (h\nu_{s,2} - h\nu_{s,1})/kT} \prod_s \frac{1 - e^{-h\nu_{s,2}/kT}}{1 - e^{-h\nu_{s,1}/kT}} \tag{11.2.7}$$

It was the development of this type of an equation for the ratio of the partition function of isotopic molecules that enabled Urey and Greiff[3] in 1935 to do their pioneering work in the calculation of isotopic exchange equilibria.

Because bond angles and bond lengths are assumed to be equal for molecules differing only in their isotopic composition, such as $H_2O^{16}$ and $H_2O^{18}$, the calculation of the ratio of certain moments of inertia becomes simplified. For example, the ratio of the moment of inertia of the $O^{18}O^{18}$ molecule to that of the $O^{16}O^{16}$ molecule is simply the ratio of their reduced masses, or 9/8. In the case of the water molecule, the ratio of the moments $I_A$, $I_B$, and $I_C$ for the two isotopic species $H_2O^{18}$ and $H_2O^{16}$ (or $D_2O$ and $H_2O$) is

$$\frac{I_{A,2}}{I_{A,1}} = \frac{m_2}{m_1}\left[\frac{1 - \dfrac{2m_2 \cos^2 \theta/2}{2m_2 + M_2}}{1 - \dfrac{2m_1 \cos^2 \theta/2}{2m_1 + M_1}}\right] \tag{11.2.8}$$

$$\frac{I_{B,2}}{I_{B,1}} = \frac{m_2 M_2}{2m_2 + M_2} \cdot \frac{2m_1 + M_1}{m_1 M_1} \tag{11.2.9}$$

$$\frac{I_{C,2}}{I_{C,1}} = \frac{m_2}{m_1} \tag{11.2.10}$$

[3] H. C. Urey and L. J. Greiff, *J. Am. Chem. Soc.*, **57**, 321 (1935).

In these equations $m$ represents the mass of the hydrogen or deuterium atom, $M$ represents the mass of the $O^{16}$ or $O^{18}$ atom. The angle $\theta$ is the bond angle of the water molecule.

As a matter of fact it is unnecessary to know the moments of inertia in order to calculate isotopic exchange equilibrium constants, as pointed out in 1947 by Urey[4] and Bigeleisen and Mayer.[5] This is because all isotopic exchange equilibrium constants would be either unity or equal to the symmetry number ratio if the classical partition functions for translation, rotation, and vibration were valid. Inasmuch as the vibrational partition functions have to be used in the quantum theory form, we need to know, therefore, only the fundamental frequencies of vibration to calculate isotopic exchange equilibrium constants. Conversely, we can conclude that the vibrations of atoms within molecules cannot be described in terms of classical equations, and that zero point energies must exist because the experimentally observed isotopic exchange equilibrium constants do differ from unity. Fundamentally, the simplification in the isotopic exchange equilibrium constant calculations stems from the Teller-Redlich product rule.[6]

For symmetrical diatomic molecules, this rule reduces to the expression

$$\frac{\omega_2}{\omega_1} = \sqrt{\frac{m_1}{m_2}} \tag{11.2.11}$$

which is of great help in calculating the frequency of the heavier molecule (which may not have been investigated spectroscopically) from the known frequency of the lighter molecule. Equation (11.2.11) can also be expressed in the more general form

$$\frac{\omega_2}{\omega_1} = \sqrt{\frac{\mu_1}{\mu_2}} \tag{11.2.12}$$

where $\mu$ is the reduced mass. This equation follows from Eq. (8.3.5), the equation of the harmonic oscillator, assuming that the potential energy curves or the potential energy of vibration is identical for

[4] H. C. Urey, *J. Chem. Soc.*, 562 (1947). See also L. Waldmann, *Naturwissenschaften*, **31**, 205 (1943).

[5] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

[6] See G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Company, Inc., New York, 1945, p. 231.

both isotopic species (the frequency of oscillation is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{11.2.13}$$

where $k$ is the so-called *force constant*).

To simplify the manipulation of (11.2.7) let us make the substitution

$$u_i = \frac{hc\omega_i}{kT} = \frac{h\nu_i}{kT} \tag{11.2.14}$$

Now, because the following equation is true (see Urey[4]),

$$\left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{I_{A,2}I_{B,2}I_{C,2}}{I_{A,1}I_{B,1}I_{C,1}}\right)^{1/2}\left(\frac{m_1}{m_2}\right)^{3n/2}\prod_s \frac{u_{s,1}}{u_{s,2}} = 1 \tag{11.2.15}$$

as well as a similar expression for diatomic molecules (see problem 18), Eq. (11.2.7) can be reduced to

$$\frac{f_2}{f_1} = \frac{Q_2^\circ}{Q_1^\circ}\left(\frac{m_1}{m_2}\right)^{3n/2} = \frac{\sigma_1}{\sigma_2}\prod_s \frac{u_{s,2}}{u_{s,1}}\cdot\frac{e^{-u_{s,2}/2}}{e^{-u_{s,1}/2}}\cdot\frac{1-e^{-u_{s,1}}}{1-e^{-u_{s,2}}} \tag{11.2.16}$$

where $m_1$ and $m_2$ are the atomic masses and $n$ the number of the isotopic atoms undergoing exchange.

In setting up the expression for the equilibrium constant of isotopic exchange equilibria such as (11.2.1), the ratio of the atomic masses cancels and we obtain the simplified expression

$$K = \frac{f^2_{H_2O^{16}} f_{CO_2^{18}}}{f^2_{H_2O^{18}} f_{CO_2^{16}}} \tag{11.2.17}$$

Bigeleisen and Mayer[5] have expanded the exponentials of (11.2.16) and made the substitution

$$\Delta u_s = u_{s,1} - u_{s,2}$$

($\Delta u_s$ is always positive), thereby obtaining

$$\ln\frac{f_2}{f_1} = \ln\frac{\sigma_1}{\sigma_2} + \sum_s\left(\frac{1}{2} - \frac{1}{u_{s,2}} + \frac{1}{e^{u_{s,2}}-1}\right)\Delta u_s \tag{11.2.18}$$

They have also calculated the function in parentheses, which they call the $G$ function, (see Appendix Table 6).

$$G = \frac{1}{2} - \frac{1}{u_{s,2}} + \frac{1}{e^{u_{s,2}}-1} \tag{11.2.19}$$

for values of $u$ between zero and 25.0. Hence if the $u_{s,1}$ and $u_{s,2}$ values are known, the isotopic exchange equilibrium constants are easily and quickly calculated.

Urey[4] has given tables of frequencies of vibration expressed in wave numbers of many molecules and their isotopic counterparts. He also listed anharmonicity correction factors, the use of which increases the accuracy of the equilibrium constant calculations.[7]

With the anharmonic terms included, Eq. (11.2.20) is written:

$$\ln \frac{f_2}{f_1} = \frac{\sigma_1}{\sigma_2} + \sum_s \left( \frac{1}{2} - \frac{1}{u_{s,2}} + \frac{1}{e^{u_{s,2}} - 1} \right) \Delta u_s - \frac{hc}{4kT} \sum_i (x_{2,ij} - x_{1,ij}) \tag{11.2.20}$$

The $x_{ij}$ term differences are summed over the $x_{11}$, $x_{22}$, $x_{33}$, $x_{12}$, $x_{13}$, $x_{23}$ components for polyatomic molecules. Some typical frequencies and anharmonicity correction factors are listed in Table 11.1. Note that $x_{ij}$ for polyatomic molecules is equivalent to $x_s\omega_s$ for diatomic molecules; i.e., in Eq. (11.2.20) substitute $x_s\omega_s$ for $x_{ij}$ when carrying out calculations for diatomic molecules. In Table 11.1 the frequencies are listed in the order $\omega_{1,s}$, $\omega_{2,s}$, $\omega_{3,s}$, the $x_{ij}$'s in the order $x_{11}$, $x_{22}$, $x_{33}$ (left vertical column), $x_{12}$, $x_{13}$, $x_{23}$ (right column), and the 2 in parentheses given after the $\omega_2$ frequency of the carbon dioxide molecule indicates the twofold degeneracy of that vibration.

Urey[4] has also calculated the ratio of partition functions and equilibrium constants at a number of temperatures for isotope exchanges involving hydrogen, lithium, boron, carbon, nitrogen, oxygen, chlorine, bromine, and iodine exchange. In the case of hydrogen isotope exchange reactions he has applied rotational corrections to the partition functions to allow for the fact that the separation of rotational levels in compounds of hydrogen is large enough relative to $kT$ to invalidate the use of the classical rotational partition function equations. We shall not discuss these corrections here.

[7] J. M. McCrea, *J. Chem. Phys.*, **19,** 48 (1951) has carried out calculations to illustrate errors in isotopic exchange equilibrium constant calculations when interaction terms are neglected and when the observed frequencies rather than zero order frequencies are used. For example, the equilibrium constant of the reaction

$$CO_2^{16} + CO_2^{18} \rightleftarrows 2CO^{16}O^{18}$$

which Urey and Greiff, *J. Am. Chem. Soc.*, **57,** 321 (1935) reported to be $3.999_0$ in 1935, at 0°C. is really $3.982_8$ when interaction is considered.

## Table 11.1
### Molecular Frequencies and Anharmonicity Correction Terms
(From Urey)

#### Diatomic molecules

| *Molecule* | $\omega_e$ | $-x_e\omega_e$ |
|---|---|---|
| $H_2$ | 4405.3 | 125.32 |
| HD | 3817.09 | 94.02 |
| $D_2$ | 3118.8 | 64.15 |
| | 3117.7 | 62.72 |
| HT | 3598.14 | 83.60 |
| DT | 2845.64 | 52.28 |
| $T_2$ | 2546.50 | 41.88 |
| $O_2^{16}$ | 1580.4 | 12.07 |
| $O_2^{18}$ | 1490.0 | 10.73 |
| $C^{12}O^{16}$ | 2167.4 | 13.28 |
| $C^{13}O^{16}$ | 2119.2 | 12.69 |
| $C^{12}O^{18}$ | 2115.2 | 12.65 |
| $N_2^{14}$ | 2359.6 | 14.45 |
| $N_2^{15}$ | 2279.6 | 13.48 |
| $N^{14}O$ | 1906.54 | 14.50 |
| $N^{15}O$ | 1872.34 | 13.99 |
| $Cl_2^{35}$ | 564.9 | 4.0 |
| $Cl_2^{37}$ | 549.4 | 3.8 |
| $Br_2^{79}$ | 323.86 | 1.07 |
| $Br_2^{81}$ | 319.84 | 1.04 |
| $I_2^{127}$ | 214.36 | 0.59 |
| $I_2^{129}$ | 212.69 | 0.58 |
| $HCl^{35}$ | 2988.95 | 51.65 |
| $DCl^{35}$ | 2143.52 | 25.56 |
| $HCl^{37}$ | 2987.5 | 51.57 |
| HI | 2309.53 | 39.73 |
| DI | 1639.45 | 20.02 |
| $HBr^{79}$ | 2649.67 | 45.21 |
| $DBr^{79}$ | 1885.95 | 22.90 |
| $HBr^{81}$ | 2646.6 | 45.19 |

#### Polyatomic molecules

| *Molecule* | $\omega_e$ | $-x_{ij}$ | |
|---|---|---|---|
| $H_2O$ | 3825.32 | 43.89 | 20.02 |
| | 1653.91 | 19.5 | 155.06 |
| | 3935.59 | 46.37 | 19.81 |
| HDO | 2820.3 | 42.27 | 89.3 |
| | 1449.4 | −4.1 | 16.0 |
| | 3882.8 | 77.39 | 25.53 |
| $D_2O$ | 2758.06 | 22.81 | 10.56 |
| | 1210.25 | 10.44 | 81.92 |
| | 2883.79 | 24.90 | 10.62 |
| DTO | 2357.1 | 27.84 | 13.53 |
| | 1117.9 | 13.7 | 9.01 |
| | 2830.7 | 41.77 | 11.3 |
| $T_2O$ | 2296.63 | 15.71 | 4.27 |
| | 1017.89 | 8.21 | 56.79 |
| | 2436.12 | 18.39 | 6.21 |
| $H_2O^{18}$ | 3815.5 | 43.66 | 19.89 |
| | 1647.8 | 19.36 | 154.03 |
| | 3919.4 | 45.99 | 19.66 |
| $D_2O^{18}$ | 2744.2 | 22.58 | 10.44 |
| | 1202.7 | 10.31 | 80.88 |
| | 2861.7 | 24.52 | 10.47 |
| $CO_2$ | 1351.20 | 0.3 | −5.7 |
| | 672.20(2) | 1.3 | 21.9 |
| | 2396.40 | 12.5 | 11.0 |
| $C^{13}O_2$ | 1351.20 | 0.30 | −5.54 |
| | 653.12(2) | 1.23 | 21.28 |
| | 2328.40 | 11.80 | 10.38 |
| $CO_2^{18}$ | 1273.92 | 0.27 | −5.29 |
| | 661.94(2) | 1.26 | 20.33 |
| | 2359.81 | 12.12 | 10.67 |

For the oxygen exchange equilibrium (11.2.1) at 273.1°K, Urey has calculated the following quantities:

$$\frac{f_{CO_2{}^{18}}}{f_{CO_2{}^{16}}} = 1.2839; \qquad \frac{f_{H_2O^{18}}}{f_{H_2O^{16}}} = 1.0741$$

The equilibrium constant for (11.2.1) with all substances in gaseous form is

$$K_1 = \frac{1.2839}{(1.0741)^2} = 1.113$$

Now, in isotopic exchange studies the experimental observations are usually given in terms of the fractionation factor $\alpha$ defined in the case of the carbon dioxide-water equilibrium by the equation

$$\alpha = \frac{\left[\frac{O^{18}}{O^{16}}\right]_{CO_2}}{\left[\frac{O^{18}}{O^{16}}\right]_{H_2O}} = \frac{\frac{2[CO_2{}^{18}] + [CO^{16}O^{18}]}{2[CO_2{}^{16}] + [CO^{16}O^{18}]}}{\frac{[H_2O^{18}]}{[H_2O^{16}]}} \qquad (11.2.21)$$

where the brackets signify moles (or molecules) of the species indicated.

Provided that the equilibrium constant of the exchange equilibrium

$$CO_2{}^{16} + CO_2{}^{18} \rightleftarrows 2CO^{16}O^{18} \qquad (11.2.22)$$

is equal to the ratio of the symmetry numbers, or 4, it is easy to show that

$$\alpha = \sqrt{K_1} \qquad (11.2.23)$$

The fractionation factor for (11.2.1) as an entirely gaseous reaction is therefore

$$\alpha = 1.055$$

In studying oxygen isotope exchange between carbon dioxide and water, it is the custom to equilibrate carbon dioxide with liquid water. For the over-all fractionation factor for the equilibrium involving liquid water,

$$CO_2{}^{16}\,(g) + 2H_2O^{18}\,(l) \rightleftarrows CO_2{}^{18}\,(g) + 2H_2O^{16}\,(l) \qquad (11.2.24)$$

the above fractionation factor must be multiplied by the fractionation factor of the equilibrium

$$H_2O^{18}\,(l) + H_2O^{16}\,(g) \rightleftarrows H_2O^{16}\,(l) + H_2O^{18}\,(g) \qquad (11.2.25)$$

which is simply the ratio of the vapor pressures of $H_2O^{18}$ to $H_2O^{16}$, or at 0°C, 0.9891. The fractionation factor of the equilibrium (11.2.24) is therefore 1.044. This theoretically expected value has been accurately confirmed by Webster, Wahl, and Urey,[8] who found 1.046 at 0°C.

The equilibrium for oxygen isotope exchange between atmospheric oxygen and water, which one might expect to be established by natural processes, apparently is not so established, as demonstrated by the frequently verified observation of Dole,[9] that the abundance of $O^{18}$ in atmospheric oxygen is 1.030 times as great as the abundance of $O^{18}$ in the oxygen of water. The calculated equilibrium value between air and ocean water is 1.014 at 25°C and 1.017 at 0°C. Apparently there is no mechanism in nature by which oxygen isotopes of atmospheric oxygen can exchange with the oxygen of water.

## 11-3. *The problem of internal rotation*

We now turn to detailed calculation of the equilibrium constant of a specific chemical reaction, namely, that of hydrogenation of ethylene to form ethane, but before doing so it is necessary to consider the effect of internal rotation within the molecule on the total partition function. We shall introduce a new partition function, that for internal rotation, or $Q_{int.\,rot.}$

Let us consider the rotation of one methyl group about the other, about an axis passing through the two carbon atoms of the molecule, and let us assume for the moment that such rotation occurs freely; that is, that there is no potential energy barrier to rotation, that the potential energy of one methyl group with respect to the other is zero at all angles of rotation (the extent to which this assumption is not valid is described below). Let $I_1$ and $I_2$ be the individual moments of inertia of each internally rotating group (these moments would be equal for the two methyl groups in ethane). Let $p_1$ and $p_2$ be the rotational momenta for the two groups; then the kinetic energy due to internal rotation $T_{int.\,rot.}$ can be expressed by

$$T_{int.\,rot.} = \frac{p_1^2}{2I_1} + \frac{p_2^2}{2I_2} \qquad (11.3.1)$$

[8] L. A. Webster, M. H. Wahl, and H. C. Urey, *J. Chem. Phys.*, **3**, 129 (1935).
[9] M. Dole, *J. Am. Chem. Soc.*, **57**, 2731 (1935); J. A. Swartout and M. Dole, *J. Am. Chem. Soc.*, **61**, 2025 (1939).

But by the laws of mechanics

$$I_1\omega_1 = p_1 = I_2\omega_2 = p_2 = p_\phi$$

hence

$$T_{int.\,rot.} = \frac{p_\phi{}^2}{2}\left(\frac{1}{I_1} + \frac{1}{I_2}\right) = \frac{p_\phi{}^2}{2I_{int.}}$$

where $I_{int.}$ is the reduced moment of inertia

$$I_{int.} = \frac{I_1 I_2}{I_1 + I_2} \tag{11.3.2}$$

The subscript $\phi$ refers to the internal angle of rotation defined in such a way that when a hydrogen atom of one methyl group lies midway between two hydrogen atoms of the second methyl group as the molecule is viewed along the C—C bond direction, the angle is zero (see Fig. 11.1).

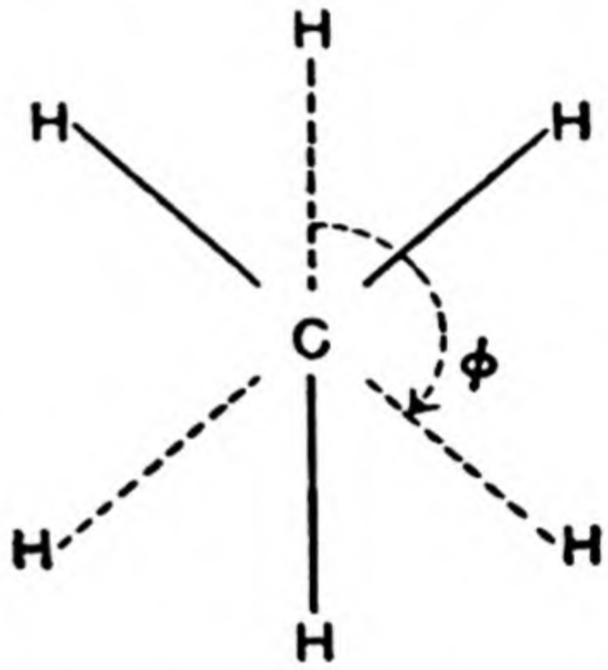



**Fig. 11.1.** Angle $\phi$ describing the extent of internal rotation in ethane.

The partition function for free internal rotation is obtained by integrating the rotational momentum $p_\phi$ from $-\infty$ to $+\infty$ and $\theta$ from 0 to $2\pi$ in the classical expression for the partition function involving a two-dimensional phase space having coordinates $p_\phi$ and $\phi$. The result is

$$Q_{int.\,rot.} = \frac{(8\pi^3 I_{int.} kT)^{1/2}}{\sigma_i h} \tag{11.3.3}$$

where $\sigma_i$, the symmetry number for internal rotation (three in the case of ethane), has been introduced.[10]

Now in most molecules involving the rotation of the methyl group, the rotation is not free, but a potential energy barrier for rotation exists. Thus the potential energy $V$ of the internally rotating system, such as that of ethane, will pass through maxima and minima as $\phi$ increases from zero to $2\pi$, as illustrated in Fig. 11.2.

[10] The derivation of Eq. (11.3.3) is given as a problem at the end of the chapter.

The curve of Fig. 11.2 may be expressed by[11]

$$V = \tfrac{1}{2}V^\circ(1 - \cos \sigma_i\phi) \tag{11.3.4}$$

or

$$V = V^\circ \sin^2 (\tfrac{1}{2}\sigma_i\phi) \tag{11.3.5}$$

Let us consider two limiting cases; first when

$$V^\circ \ll kT$$

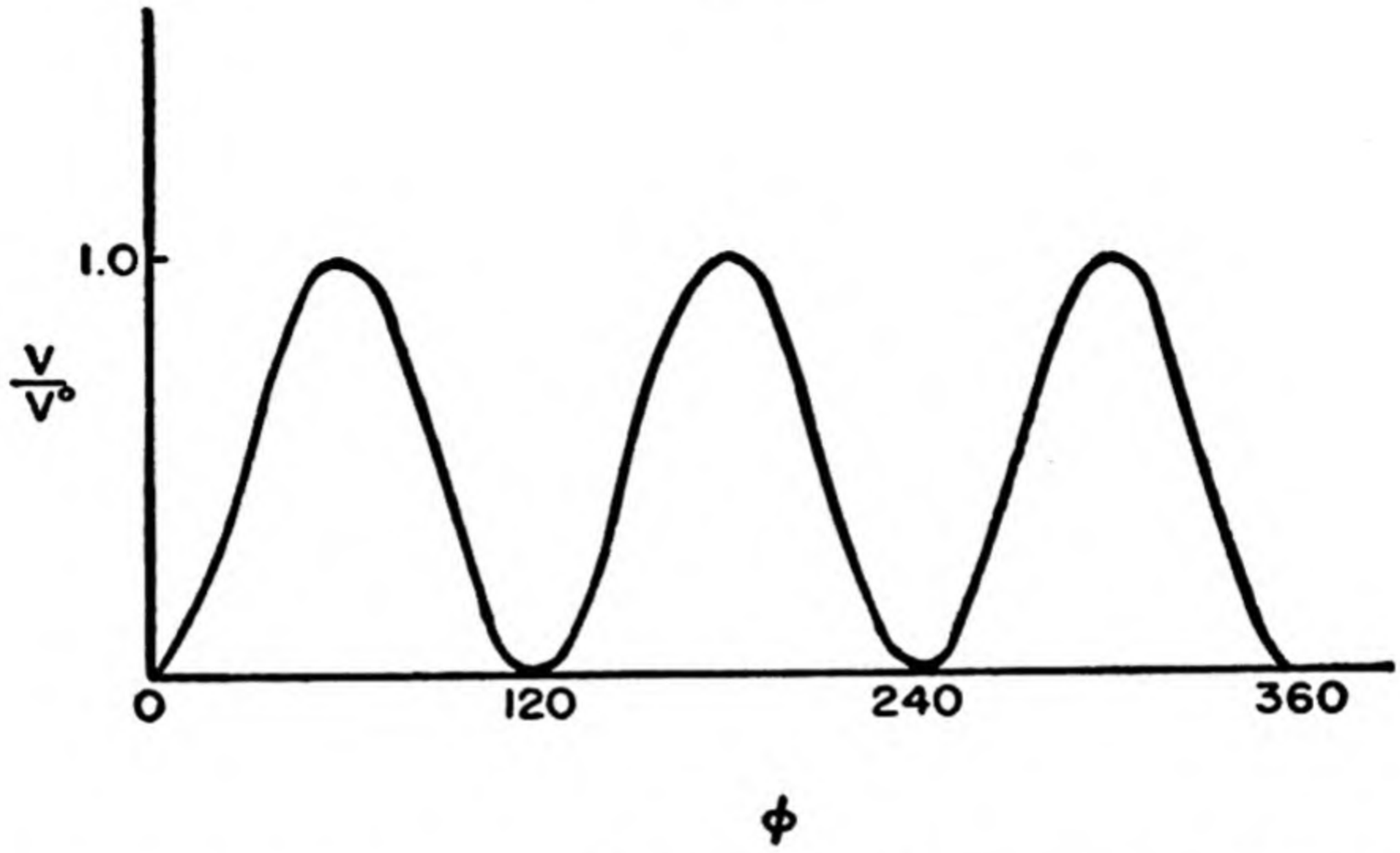



**Fig. 11.2.** Hypothetical potential energy diagram for internal rotation in ethane.

we have the situation of free rotation which has been treated above. If

$$V^\circ \gg kT$$

we may consider that rotation as such ceases, and we have instead a rotatory vibration or oscillation about the position of minimum potential energy. For small values of $\phi$, we can write in this case

$$V = V^\circ(\tfrac{1}{2}\sigma_i\phi)^2 \tag{11.3.6}$$

This is equivalent to a vibration of frequency $\nu_i$ given by the equation

$$\nu_i = \frac{\sigma_i(V^\circ/2I)^{1/2}}{2\pi} \tag{11.3.7}$$

To understand this, let us refer again to the equation for the potential energy of the linear harmonic oscillator,

$$V = 2\pi^2\nu^2\mu q^2 \tag{8.3.3}$$

[11] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, London, 1939, p. 108.

For an oscillation we may equate $\mu q^2$ to $I\phi^2$ and write

$$V = 2\pi^2\nu_i^2 I\phi^2 = V^\circ(\tfrac{1}{2}\sigma_i\phi)^2$$

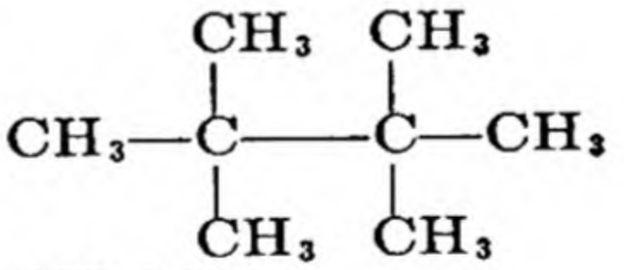
Solving for $\nu_i$, we obtain (11.3.7).

However, situations intermediate between the two extremes of $V^\circ$ being much greater or much less than $kT$ are of great importance, since $V^\circ$ is of the order of magnitude of $kT$ for a vast number of organic molecules. Unfortunately, no simple treatment can be derived for this case, but Pitzer[12] and his co-workers have succeeded in solving the problem by an approximation method. Table 11.2 contains a list of potential barriers for internal rotation estimated by the method of Pitzer. This method consists in calculating the entropy, assuming free rotation, and then, knowing the difference between the calculated entropy and the observed entropy, the height of the potential barrier can be estimated from tables in which the entropy difference is given as a function of the internal rotational partition function and $V^\circ/RT$. Differences in free energy, heat content, and heat capacity are also tabulated.

TABLE 11.2

RESTRICTED ROTATION POTENTIAL ENERGY BARRIERS

($V^\circ$ in cal./mole)

| *Substance* | $V^\circ$ | *Substance* | $V^\circ$ |
|---|---|---|---|
| $CH_3—C\equiv C—CH_3$ | 0 |  | 4700 (ave.) |
| Toluene | <1000 | | |
| *m* and *p*-xylene | <1000 | | |
| $CH_3CH=CHCH_3$ | 2000 | | |
| $CH_3CH=CH_2$ | 2120 | $CH_3OH$ | 1000 |
| $CH_3CH_3$ | 2750 | $CH_3CH_2OH$ | 800 [C—O axis] |
| $CH_3CH_2CH_3$ | 3400 | | 3300 [C—C axis] |
| $(CH_3)_4C$ | 4500 | $CH_3CH_2Cl$ | 3700 |

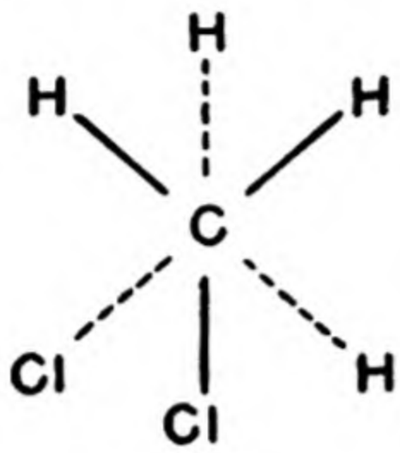
Halford[13] has shown how the thermodynamic functions for this internal rotation may be calculated by a method different from and simpler than that of Pitzer and Gwinn. He has checked the tabulations of Pitzer and Gwinn at several points, and has shown how to extend the calculations to molecules having low potential barriers for internal rotation.

[12] K. S. Pitzer, *J. Chem. Phys.*, **5,** 469 (1937); K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10,** 428 (1942); **16,** 303 (1948); K. S. Pitzer, *Chem. Revs.*, **27,** 39 (1940); K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39,** 435 (1946).

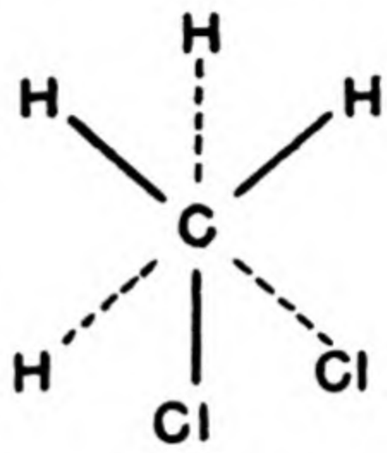
[13] J. O. Halford, *J. Chem. Phys.*, **15,** 645 (1947); **16,** 410 (1948); **18,** 444 (1950).

At this point it is of some interest to consider the concept of "rotational isomers" introduced by Mizushima, Morino, and co-workers.[14]

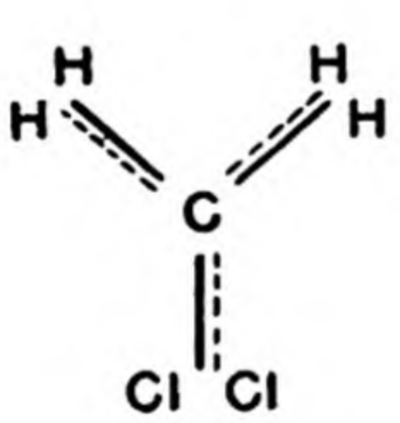
If a compound such as 1,2-dichlorethane is viewed along the C—C bond direction, *trans*, *cis*, and *gauche* configurations are possible and are called rotational isomers by Mizushima. In Fig. 11.3, forms (*c*) and (*d*) are, of course, equivalent energetically. Mizushima has been able to show from a study of Raman and



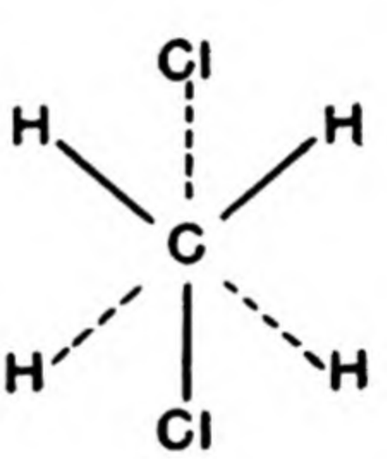

(c) Gauche




(d) Gauche




(a) Cis




(b) Trans

**Fig. 11.3.** The rotational isomers of 1,2 dichloroethane.

infrared spectra that in the solid state all the 1,2-dichlorethane is in the *trans* form, but that in the liquid and gaseous state both the *trans* and the *gauche* forms are present. No evidence for the *cis* form exists, and it may be ruled out of consideration. (The substance 2,2-dimethylbutane has only one possible molecular form and does not show the spectral changes on solidification that 1,2-dichlorethane exhibits.)

Mizushima estimates the difference in energy between the *gauche* and *trans* forms to be 1.2 kg.cal./mole. (This is not to be identified with the potential barrier for rotation, which is about 3.0 kg.cal./

[14] S. Mizushima, Y. Morino, and M. Takeda, *J. Chem. Phys.*, **9**, 826 (1941); S. Mizushima *et al.*, *J. Chem. Phys.*, **7**, 591 (1949); **19**, 1477 (1951).

mole.) In solution the *gauche* form is favored because its dipole moment causes a dipole-induced dipole interaction with the solvent, which lowers the energy of the *gauche* form.

## 11-4. *Detailed calculation of a chemical equilibrium constant*

Guggenheim[15] has described in rather complete detail his calculation of the equilibrium constant $K_p$, at a number of temperatures, of the reaction

$$C_2H_4 + H_2 \rightleftarrows C_2H_6 \tag{11.4.1}$$

At the high temperatures at which the experimental studies of this equilibrium have been carried out (from 400 to 700°C) and at 1 atmosphere pressure (the standard state) we may safely treat all gases as perfect gases. The equilibrium constant will be given in terms of the partition function by the equation

$$K = \frac{Q^\circ_{C_2H_6}/N}{(Q^\circ_{H_2}/N)(Q^\circ_{C_2H_4}/N)} \tag{11.4.2}$$

and

$$\Delta F^\circ = F^\circ_{C_2H_6} - F^\circ_{C_2H_4} - F^\circ_{H_2} \tag{11.4.3}$$

In the case of hydrogen, the vibrational energy states above the ground state will have a negligible contribution, so that

$$\frac{F^\circ_{H_2}}{RT} = -\ln \frac{Q^\circ_{trans.} Q^\circ_{rot.}}{N} \tag{11.4.4}$$

The refinement of considering stretching due to centrifugal force during rotation is negligible; the refinement of allowing for the effect of quantization of the rotational motion can be absorbed into the partition function factor for the energy zero. Guggenheim made use of the physical constants of the different molecules given in Table 11.3.

TABLE 11.3

PHYSICAL CONSTANTS FOR HYDROGEN, ETHYLENE, AND ETHANE

| *Gas* | $M$ | $\sigma$ | $\sigma_i$ | $I^*$ | $I_A^*$ | $I_B^*$ | $I_C^*$ |
|---|---|---|---|---|---|---|---|
| $H_2$ | 2.018 | 2 | | 0.46 | | | |
| $C_2H_4$ | 28.03 | 4 | | | 5.7 | 27.5 | 33.2 |
| $C_2H_6$ | 30.05 | 6 | 3 | | $10.7_4$ | $40.0_9$ | $40.0_9$ |

* In g. cm.$^2$ $\times 10^{40}$

[15] E. A. Guggenheim, *Trans. Faraday Soc.*, 37, 97 (1941).

Using the constants of Table 11.3, it is easy to calculate the value of $F^\circ/RT$ for hydrogen.

Because the translational and rotational partition function ratio

$$\frac{(Q^\circ_{trans.}Q^\circ_{rot.})_{C_2H_6}}{(Q^\circ_{trans.}Q^\circ_{rot.})_{C_2H_4}}$$

reduces to a ratio of constants independent of the temperature

$$\left(\frac{M_{C_2H_6}}{M_{C_2H_4}}\right)^{3/2} \frac{\sigma_{C_2H_4}}{\sigma_{C_2H_6}} \cdot \frac{(I_A I_B I_C)^{1/2}_{C_2H_6}}{(I_A I_B I_C)^{1/2}_{C_2H_4}}$$

Guggenheim found it convenient to calculate $F^\circ_{C_2H} - F^\circ_{C_2H_4}$ rather than the individual free energies.

The most serious problems in connection with calculation of the partition functions of ethylene and ethane were found in assignment and evaluation of the frequencies of the different modes of vibration, which number 12 for ethylene and 18 for ethane. Eleven of the modes for ethylene can be determined spectroscopically, but the remaining one, the twisting mode, is completely inactive in both the Raman and infrared. Its frequency has to be assigned so as to make the heat capacity calculations by means of the partition function agree with the observed heat capacity values. Table 11.4 contains the 12 estimated frequencies of ethylene.[16]

TABLE 11.4

NORMAL MODES OF ETHYLENE

| *Symmetry class* | *Symbol* | $\omega_i$ (cm.$^{-1}$) | *Symmetry class* | *Symbol* | $\omega_i$ (cm.$^{-1}$) |
|---|---|---|---|---|---|
| $A_{1g}$ | $\nu_2$ | 3019 | $B_{2g}$ | $\nu_6$ | 3069 |
| | $\nu_4$ | 1623 | | $\nu_{10}$ | 950 |
| | $\nu_8$ | 1342 | $B_{2u}$ | $\nu_{11}$ | 940 |
| $A_{1u}$* | $\nu_7$ | [900] | $B_{3g}$ | $\nu_{12}$ | 1100 |
| | $\nu_1$ | 2988 | | $\nu_5$ | 3107 |
| $B_{1u}$ | $\nu_3$ | 1444 | $B_{3u}$ | $\nu_9$ | 950 |

* This is the twisting mode.

Sixteen of the 18 modes of ethane are known fairly reliably, one of the remaining does not occur as a fundamental so that Guggenheim refers to it as "the uncertain frequency." The remaining mode is the twisting mode, and analogously to the twisting mode of ethylene, is spectroscopically inactive. The heat capacity data of

[16] The frequency values used by Guggenheim are those from a paper by Bonner, *J. Am. Chem. Soc.*, **58,** 34 (1936) in the case of ethylene, and by Crawford, Avery, and Linnett, *J. Chem. Phys.*, **6,** 682 (1938) in the case of ethane.

ethane are consistent with a twisting potential energy of the form of Eq. (11.3.5) with $V°/k$ equal to 1570°K and $\sigma_i$ equal to 3.

TABLE 11.5

NORMAL MODES OF ETHANE

| SINGLE MODES | | DOUBLY DEGENERATE MODES | |
|---|---|---|---|
| *Symmetry class* | $\omega_i$ (cm.$^{-1}$) | *Symmetry class* | $\omega_i$ (cm.$^{-1}$) |
| $A'_1$ | 993 | | 827 |
| | 1375 | $E'$ | 1480 |
| | 2927 | | 2980 |
| $A'_2$ | 1380 | | [1120] (uncertain) |
| | 2926 | $E''$ | 1460 |
| $A''_1$ | Twisting mode | | 2970 |

In Table 11.5 are collected the values of the frequencies (in wave numbers) of the fundamental modes of ethane. Guggenheim calculated the contribution of the twisting mode to the free energy by first assuming free rotation and then adding a correction term because of the restriction to rotation. He interpolated from the tables prepared by Pitzer[12] for the correction term.

In order to obtain the partition function factor for the energy zero, the factor of greatest importance in the calculation of the

TABLE 11.6

THERMODYNAMIC FUNCTIONS FOR THE HYDROGEN-ETHYLENE-ETHANE EQUILIBRIUM

| *Temperature* (°C) → | 400 | 500 | 600 | 700 |
|---|---|---|---|---|
| | | $\Delta H/RT$ | | |
| Hydrogen | 3.50 | independent of temperature | | |
| Ethane-ethylene | | | | |
| Translation + rotation | 0 | | | |
| Ethylene | | | | |
| 11 certain modes | 1.65 | 2.06 | 2.45 | 2.83 |
| Twisting mode | 0.33 | 0.39 | 0.44 | 0.48 |
| Ethane | | | | |
| 15 certain modes | 2.00 | 2.53 | 3.04 | 3.54 |
| pair of "uncertain modes" | 0.48 | 0.60 | 0.70 | 0.79 |
| Internal free rotation | 0.50 | 0.50 | 0.50 | 0.50 |
| Effect of restriction | 0.29 | 0.29 | 0.29 | 0.29 |
| $\frac{\Delta H - \Delta E_0^\circ}{R} \times 10^3$ | 1.49 | 1.57 | 1.62 | 1.65 |
| $-\frac{\Delta H}{R} \times 10^3$ | 17.01 | 17.09 | 17.14 | 17.17 |

TABLE 11.6 (*Con't*)

THERMODYNAMIC FUNCTIONS FOR THE HYDROGEN-ETHYLENE-ETHANE EQUILIBRIUM

| *Temperature* (°C) → | 400 | 500 | 600 | 700 |
|---|---|---|---|---|
| | | $-(F^\circ - E_0^\circ)/RT$ | | |
| **Hydrogen** | | | | |
| Translation | 13.68 | 14.02 | 14.33 | 14.60 |
| Rotation | 1.36 | 1.51 | 1.63 | 1.74 |
| Total | 15.04 | 15.53 | 15.96 | 16.34 |
| **Ethane-ethylene** | | | | |
| Translation | 0.10 | independent of temperature | | |
| Rotation | 0.20 | | | |
| Translation + rotation | 0.30 | | | |
| **Ethylene** | | | | |
| 11 certain modes | 0.67 | 0.93 | 1.21 | 1.49 |
| Twisting mode | 0.16 | 0.21 | 0.26 | 0.31 |
| Total vibrational | 0.83 | 1.14 | 1.47 | 1.80 |
| **Ethane** | | | | |
| 15 certain modes | 0.81 | 1.12 | 1.45 | 1.81 |
| Pair of "uncertain modes" | 0.20 | 0.27 | 0.35 | 0.43 |
| Internal free rotation | 1.38 | 1.45 | 1.51 | 1.57 |
| Effect of restriction | −0.53 | −0.49 | −0.45 | −0.42 |
| Total vibrational | 1.86 | 2.35 | 2.86 | 3.39 |
| **Ethane-ethylene** | | | | |
| -Hydrogen | −13.71 | −14.02 | −14.27 | −14.45 |
| $-\Delta E_0^\circ/RT$ | 23.06 | 20.08 | 17.78 | 15.95 |
| $-\Delta F_0^\circ/RT$ | 9.35 | 6.06 | 3.51 | 1.50 |
| $K_P$ (calculated) | 11,000 | 430 | 33.5 | 4.5 |
| $K_P$ (observed) | 12,000[a] | 420[a] | 32.[c] | 5.0[c] |
| | | 320[b] | | |

[a] Frey and Huppke, *Ind. Eng. Chem.*, **25,** 54 (1933), as reinterpreted by Kistiakowsky *et al.*

[b] Videnski and Vinikova, *J. Gen. Chem. Moskow,* **4** [46], 120 (1934).

[c] Pease and Durgan, *J. Am. Chem. Soc.*, **50,** 2715 (1928).

equilibrium constant, he used the method already described in Chapter 9, Eq. (9.6.14). Adopting the value of the heat of reaction (11.4.1) found experimentally by Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan[17] at 78°C., or −32,830 cal./mole, he found $\Delta E_0^\circ$ to be −30,840 cal./mole. Table 11.6 gives a summary of Guggenheim's calculations at 400, 500, 600, and 700°C, along with the experimentally measured values of $K_P$. The agreement is excellent, with differences well within the experimental limits of

[17] *J. Am. Chem. Soc.*, **57,** 65 (1935).

error. In fact, the statistical thermodynamic calculation of $K_P$ probably gives values more reliable than the experimental ones.

Another chemical equilibrium of considerable interest is the thermal dissociation of molecular hydrogen

$$H_2 \rightleftarrows 2H \tag{11.4.5}$$

In the evaluation of the partition function of $H_2$ it is necessary to sum over all rotational and vibrational states by means of the equation

$$Q_{rot.,\,vib.} = \sum_{v=0}^{\infty} \tfrac{1}{2}g(g \pm 1) \sum_{j=0}^{\infty} 2(j+1)e^{-\epsilon(v,j)/kT} \tag{11.4.6}$$

where

$$\epsilon(v,j) = \epsilon_v + B_v(j+\tfrac{1}{2})^2 - D_v(j+\tfrac{1}{2})^4 + H_v(j+\tfrac{1}{2})^6 \tag{11.4.7}$$

$$D_v = +0.0465 - 0.00135(v+\tfrac{1}{2})$$

$$H_v = 5.18 \times 10^{-5}$$

and $\epsilon_v$ and $B_v$ have the following values[18] (cm.$^{-1}$).

| $v$ | $\epsilon_v$ | $B_v$ |
|---|---|---|
| 0 | 0 | 59.354 |
| 1 | 4161.96 | 56.404 |
| 2 | 8083 | 53.630 |
| 3 | 11,778.5 | 50.834 |
| 4 | 15,247.5 | 48.008 |

Now

$$\frac{F^\circ - E_0^\circ}{T} = -\frac{3}{2}R\ln M - \frac{5}{2}R\ln T + R\ln P - R\ln Q_i + 7.2767$$

[18] These are the values used by W. F. Giauque, *J. Am. Chem. Soc.*, **52**, 4817 (1930). A more up-to-date equation would express the rotational energies in terms of $j(j+1)$ instead of $(j+1)^2$; e.g.,

$$\epsilon_{(v,j)} = G(v) + F(j)$$

$$G(v) = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \omega_e y_e(v+\tfrac{1}{2})^3 + \cdots$$

$$F(j) = B_v j(j+1) - D_v j^2(j+1)^2 + H_v j^3(j+1)^3 + \cdots$$

with the following values for the constants as given by G. Herzberg, *Can. J. Research*, **28A**, 144 (1950):

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \cdots$$

$$D_v = D_e + \beta_e(v+\tfrac{1}{2}) + \cdots$$

$$B_e = 60.809; \quad \alpha_e = 2.993 + 0.025(v+\tfrac{1}{2})^2; \quad \gamma_e = 0.0247$$

$$H_v = 5.18 \times 10^{-5}; \quad D_e = 0.04648; \quad \beta_e = -0.00134$$

$$\omega_e = 4395.24; \quad \omega_e x_e = 117.995; \quad \omega_e y_e = 0.29_3$$

which at 1000°K yields

$$\frac{F^\circ - E_0^\circ}{T} = -2.050 - 34.27 + 0 - 6.45 + 7.2767$$
$$= -35.507$$

The partition function for monatomic hydrogen is simply the translational partition function multiplied by the nuclear and electronic spin weights, or

$$\frac{F^\circ - E_0^\circ}{T} = -\frac{3}{2} R \ln (1.008) - \frac{5}{2} R \ln T - R \ln 4 + 7.2767$$

At 1000°K this equals −29.830. Hence for the dissociation

$$H_2 \rightleftarrows 2H$$

$$\frac{\Delta(F^\circ - E_0^\circ)}{T} = 2(-29.830) - (-35.507) = -24.153$$

The zero of energy term, $E_0^\circ$ is 102,800 cal./mole; hence

$$R \ln K = -\frac{\Delta E_0^\circ}{T} - \frac{\Delta(F^\circ - E_0^\circ)}{T}$$
$$= -\frac{102{,}800}{1000} + 24.153 = -78.647$$

or $$K = 6.3 \times 10^{-18} \quad \text{at } 1000°K$$

Table 11.7 contains a comparison of observed and calculated values of the dissociation constant of $H_2$. The calculated values are those of Giauque,[19] who has summarized the data of a number of investigators.

TABLE 11.7

THE DISSOCIATION CONSTANT OF $H_2$

| | | Experimental | | |
|---|---|---|---|---|
| *T* (°K) | *Dissociation calculated* (%) | *Langmuir* | *Saha* | *Edgar* |
| 2000 | 0.086 ± 0.0011 | 0.17 | 1 | 0.63 |
| 3000 | 8.1 | 7.2 | 46 | 26 |
| 3500 | 29.7 | 21 | 85 | |
| 4000 | 63.3 | | 96 | |
| 5000 | 95.7 | | 100 | |

[19] W. F. Giauque, *J. Am. Chem. Soc.*, **52,** 4829 (1930); I. Langmuir, *J. Am. Chem. Soc.*, **34,** 860, 1310 (1912); **36,** 1708 (1914); **37,** 417 (1915); M. N. Saha, *Phil. Mag.*, **40,** 483 (1920); G. Edgar, *J. Am. Chem. Soc.*, **45,** 673 (1923). Saha's and Edgar's values were calculated from earlier experimental data of others.

Considering the great variation in the experimental results, and the experimental difficulties in obtaining them, it is undoubtedly safe to conclude that the calculated thermal dissociation constants of hydrogen are far more accurate than the experimental data.

## PROBLEMS

**1.** Write the complete partition function for the neutron (spin equals 1/2), and for methane.

**2.** Compute the equilibrium constant for the reaction producing phosgene at 100°C.

$$CO + Cl_2 \rightleftarrows COCl_2$$

**3.** Compute the equilibrium constant for the hydrolysis of phosgene (in the vapor state) at 100°C.

$$COCl_2 + H_2O \rightleftarrows 2HCl + CO_2$$

**4.** Discuss the dissociation of HCl and DCl into atoms at 250°C, and calculate the ratio of the equilibrium constant for the dissociation of HCl to that for DCl.

**5.** Compute the dissociation constant at 300°K of the gaseous reaction

$$NaCl \rightleftarrows Na^+ + Cl^-$$

Assume that all species act like perfect gases. $\Delta\epsilon_0^\circ$ is $8.63 \times 10^{-12}$ ergs per molecule, and the distance between the sodium and chlorine nuclei is $2.37 \times 10^{-8}$ cm. The vibrational frequency is so high that the vibrational partition function may be taken as unity.

**6.** Repeat Problem 5 after dividing $\Delta\epsilon_0^\circ$ by 80, the dielectric constant of water.

**7.** Compute the equilibrium constant at 1000°K of the dissociation

$$Na_2 \rightleftarrows 2Na$$

making use of the following data: $\omega = 159.23$ cm.$^{-1}$; $r = 3.078 \times 10^{-8}$ cm.; $\epsilon_0^\circ$ 0.73 electron volt (1 e.v. = 8106 cm.$^{-1}$); $h = 6.624 \times 10^{-27}$ erg sec.; $c = 2.998 \times 10^{10}$ cm./sec.; $k = 1.3805 \times 10^{-16}$ erg/molecule degree.

**8.** Making use of partition function equations, derive the equation for the variation with temperature, $\partial \ln K/\partial T$, of the equilibrium constant of the *cis-trans* isomerization of 1,2-dichloroethylene for temperatures such that $h\nu \gg kT$.

**9.** Calculate the equilibrium constant of the following reaction at 273°K:

$$O_2^{16} + O_2^{18} \rightleftarrows 2O^{16}O^{18}$$

**10.** Prove that if $K$ for the equilibrium (11.2.22) is 4, then $\sqrt{K} = \alpha$, where $K$ is the equilibrium constant of reaction (11.2.1) and $\alpha$ is the fractionation factor defined by Eq. (11.2.21).

**11.** Compute the equilibrium constant for the isotopic exchange equilibrium at 0°C.

$$2H_2O^{18}\ (l) + O_2^{16}\ (g) \rightleftarrows 2H_2O^{16}\ (l) + O_2^{18}\ (g)$$

**12.** Calculate the equilibrium constant of the reaction at 300°K.

$$N_2^{14} + 2N^{15}O \rightleftarrows N_2^{15} + 2N^{14}O$$

**13.** Calculate at 400°K the equilibrium constant of the reaction

$$H_2O^{18}\ (g) + NO^{16}\ (g) \rightleftarrows H_2O^{16}\ (g) + NO^{18}\ (g)$$

**14.** Using the two-dimensional phase space having coordinates $p_\phi$ and $\phi$, derive Eq. (11.3.3) according to classical methods.

**15.** The solution of the wave equation for the case of free internal rotation leads to the energy levels

$$\epsilon_r = \frac{h^2}{32\pi^2 I_{int.}} r^2$$

where $I_{int.}$ is the reduced moment of inertia and $r$ is the quantum number for internal rotation. Show how Eq. (11.3.3) may be obtained from this equation.

**16.** Compute the r.m.s. angular momentum of an internal rotator whose energy is given by the expression $p_\phi^2/2I_{int.}$.

**17.** The products of the principal moments of inertia are $2.012 \times 10^6$ and $2.647 \times 10^6$ for the *trans* and *gauche* forms, respectively, of 1,2-dichlorethane in atomic weight angstrom units. The most significant skeletal vibration frequences are 300, 223, 709, 754, and 1052 cm.$^{-1}$ for the *trans* form, and 265, 411, 654, 677, and 1031 cm.$^{-1}$ for the *gauche* form. The difference in $E_0^\circ$ for the two forms is 1.2 kg. cal./mole, with the *gauche* form having the greater energy content. Calculate the ratio of *gauche* to *trans* isomers at 400°C.

**18.** Prove the correctness of Eq. (11.2.15) by applying it to the special case of the isotopic pair $HCl^{35}$, $HCl^{37}$. (No numerical calculations need be made in this proof.)

# *Chapter 12*

# ENTROPY OF CHEMICAL SUBSTANCES

12-1. The Entropy of Hydrogen. 12-2. The Entropy of Water and Other Inorganic Compounds. 12-3. The Entropy of Ethane and Other Hydrocarbons. 12-4. Corrections to the Entropy for Nonideal Gas Behavior.

## 12-1. *The entropy of hydrogen*

During the first half of the twentieth century the entropy of hydrogen was the subject of a number of investigations. Table 12.1 gives the results of the experimental measurements of the increase in entropy of hydrogen from $-273$ to 25°C, and in its standard state (1 atmosphere pressure).

Table 12.1

The Calorimetric Entropy of Hydrogen at 25°C

| | |
|---|---|
| Solid: 0–13.95°K (Debye function) | 0.52 e.u. |
| Entropy of fusion: 28.0/13.95 | 2.01 |
| Entropy of vaporization: 217.8/13.95 | 15.61 |
| Correction for gas imperfection | 0.03 |
| Compression: 5.38 cm. to 76 cm. | −5.26 |
| Entropy of heating to 298.1°K $\int_{13.95}^{298.1} C_p d \ln T$ | 16.73 |
| Total calorimetric entropy* at 298°K | 29.64 ± 0.1 e.u. |

* For the calorimetric entropy of hydrogen, see W. F. Giauque, *J. Am. Chem. Soc.*, **52,** 4823 (1930). This paper also includes the calculation of the statistical thermodynamic entropy and other functions of hydrogen. See also R. H. Sherman and W. F. Giauque, *J. Am. Chem. Soc.*, **75,** 2007 (1953).

The entropy of hydrogen calculated by statistical thermodynamics gives at 25°C,

| | |
|---|---|
| Translational contribution = | 28.090 e.u. |
| Rotational and vibrational = | 5.889 |
| Total calculated entropy | 33.979 e.u.[1] |

[1] The 1953 revised calculation yielded 33.96 e.u.

This calculated entropy is considerably greater than the observed, the difference being 4.34 e.u., which is far beyond the uncertainties in either the experimental observations or the theoretical calculations. Obviously, some additional factor in interpretation of the experimental entropy value has to be considered, and this is just the increase in entropy due to the mixing of *ortho*- with *para*-hydrogen. In the calculation of the statistical thermodynamic entropy given above, the spin weights of the nuclei have been considered, as well as rotational weights of both the *ortho* and *para* forms. Entropy factors due to the mixing of the hydrogen isotopes with each other have not been included, because the convention has been adopted of omitting isotopic mixing contributions to the entropy. For most elements the relative proportions of the isotopes are not changed much in chemical reactions; when they do change, the effect of the isotopic shifts can be calculated by the methods of the previous chapter. For example, consider the mixing of $O_2^{16}$ with $O_2^{18}$. The entropy of this process is given by the entropy of mixing equation

$$S_{mix.} = -R \sum_i N_i \ln N_i \qquad (12.1.1)$$

For the mixing of one mole of $O_2^{16}$ with one mole of $O_2^{18}$ we have

$$S = -R(\ln \tfrac{1}{2} + \ln \tfrac{1}{2}) = R \ln 4$$

If we calculate the equilibrium constant of the isotopic exchange equilibrium,

$$O_2^{16} + O_2^{18} \rightleftarrows 2O^{16}O^{18}$$

we also find $S = R \ln 4$ (because for reactions in which $\Delta H = 0$, $\Delta F^\circ = -T\Delta S^\circ$, and $\Delta S^\circ = R \ln K$).

Now let us turn to the consideration of the effect of nuclear spin on the entropy of hydrogen. We can proceed either through calculation of the entropy of mixing or through the equation relating the statistical weight directly to the entropy,

$$S_{weight} = R \ln g_a g_b + R \ln (2j + 1) \qquad (12.1.2)$$

In Eq. (12.1.2) we have included in the statistical weight contribution to the entropy, the nuclear spin weight and the rotational weight, but have omitted the electronic weight. If this is other than unity, we shall also have to consider it.

For hydrogen in the ground or lowest rotational state, the spin weight for each of the two nuclei is 2, but the rotational weight for the *ortho*- is 3 and that for *para*-hydrogen is unity. Remember that on cooling normal temperature hydrogen to low temperature the relative proportion of *ortho* to *para* remains at 3 to 1, so that in 1 mole of hydrogen there is 3/4 mole of *ortho* and 1/4 mole of *para*-hydrogen. The various contributions to the entropy of hydrogen close to the absolute zero can therefore be listed as follows:

*Ortho.*

$$S_{nuclear\ spin\ wt.} = R \ln \tfrac{1}{2}[g(g+1)] = R \ln 3 \qquad (12.1.3)$$

$$S_{rot.\ wt.} = R \ln (2j+1) = R \ln 3$$

*Para.*

$$S_{nuclear\ spin\ wt.} = R \ln \tfrac{1}{2}g(g-1) = 0 \qquad (12.1.4)$$

$$S_{rot.\ wt.} = R \ln (2j+1) = 0$$

*Mixing Ortho and Para* (for one mole total of hydrogen).

$$S_{mix.} = -\tfrac{3}{4}R \ln \tfrac{3}{4} - \tfrac{1}{4}R \ln \tfrac{1}{4}$$

*Total Entropy Due to Weights and Mixing.*

$$S = \tfrac{3}{4}R \ln 3 + \tfrac{3}{4}R \ln 3 - \tfrac{3}{4}R \ln \tfrac{3}{4} - \tfrac{1}{4}R \ln \tfrac{1}{4}$$

or

$$S = R \ln 4 + \tfrac{3}{4}R \ln 3 = 4.39 \text{ e.u.}$$

Subtracting 4.39 from the previously calculated value of 33.96, we obtain 29.57, i.e., in almost perfect agreement with the observed calorimetric entropy of 29.64 e.u. This calculation might also have been carried out by considering that the entropy of normal hydrogen at very low temperatures is increased by the entropy of mixing 3 parts of *ortho*, which itself consists of 9 separate types (molecules with 3 different nuclear and 3 different rotational symmetric wave functions or nine possible combinations). The mole fraction of each type of *ortho*-hydrogen is 1/12, therefore, and the entropy of mixing becomes

$$S = -\tfrac{3}{4}R \ln \tfrac{1}{12} - \tfrac{1}{4}R \ln \tfrac{1}{4}$$

This also equals

$$R \ln 4 + \tfrac{3}{4}R \ln 3$$

as above.

For both hydrogen and deuterium, the spin weight entropy plus the entropy of mixing the *ortho* and *para* forms is

$$R \ln g^2 \qquad (12.1.5)$$

For a heteronuclear compound, the spin weight entropy is

$$R \ln g_a g_b \qquad (12.1.6)$$

Thus the spin weight entropy of the homonuclear compounds $H_2$ and $D_2$, plus the entropy of mixing, is equal to the spin weight entropy given by (12.1.6) if we consider each nucleus in the $H_2$ and $D_2$ molecules separately as we do in the heteronuclear compound.

Now in chemical reactions, the nuclear spin weights remain constant; hence it is customary to omit them from the total entropy, since they would not contribute anything to the change of entropy in a chemical reaction. The entropy to use in thermodynamic calculations is therefore neither the total calculated statistical thermodynamic entropy nor the measured calorimetric entropy, but the so-called "spectroscopic entropy," or the statistical thermodynamic entropy from which the nuclear spin entropy has been subtracted, e.g.,

$$\text{spectroscopic entropy} = \text{total entropy} - \text{nuclear spin entropy} \qquad (12.1.7)$$

In Eq. (12.1.7) by nuclear spin entropy we mean $R \ln g_a g_b$ for heteronuclear compounds and $R \ln g^2$ for homonuclear compounds.

The difference between the spectroscopic entropy and the calorimetric entropy is the entropy due to the rotational weight; in the case of hydrogen this is

$$S_{rot.wt.} = \underset{ortho\ (j=1)}{\tfrac{3}{4}R \ln (2j+1)} + \underset{para\ (j=0)}{\tfrac{1}{4}R \ln (2j+1)} = \tfrac{3}{4}R \ln 3$$

## 12-2. *The entropy of water and other inorganic compounds*

In addition to molecular hydrogen, other compounds exist in which the calculated entropy fails to agree with the calorimetric entropy even after subtraction of the nuclear spin weight entropy from the statistical thermodynamic entropy. Table 12.2 lists a number of inorganic substances with their calorimetric and spectroscopic entropies.[2]

For the most part there is excellent agreement between the observed entropy and the calculated entropy after correction for the orientational weights. In the case of CO the correction factor is

[2] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, London, 1939, pp. 211, 213.

TABLE 12.2

ENTROPIES OF INORGANIC GASEOUS SUBSTANCES AT 25°C AND 1 ATMOSPHERE

| *Substance* | *Observed calorimetric entropy* | *Spectroscopic entropy (Calculated entropy—nuclear spin entropy)* | *Calculated calorimetric entropy* | *Correction factor* |
|---|---|---|---|---|
| $H_2$ | 29.64 | 31.21 | 29.57 | $-\frac{3}{4}R \ln 3$ |
| $D_2$ | 33.9 | 34.62 | 33.88 | $-\frac{1}{3}R \ln 3$ |
| $N_2$ | 45.9 | 45.79 | | |
| $O_2$ | 49.1 | 49.03 | | |
| HCl | 44.5 | 44.64 | | |
| CO | 46.2 | 47.32 | 45.93 | $-R \ln 2$ |
| (121°K) NO | 43.0 | 43.75 | 43.06 | $-\frac{1}{2}R \ln 2$ |
| $N_2O$ | 47.36 | 48.50 | 47.12 | $-R \ln 2$ |
| $CH_4$ at | 36.53 | 36.61 | | |
| $CH_3D$ boiling | 36.72 | 39.49 | 36.73 | $-R \ln 4$ |
| $H_2S$ points | 46.38 | 46.44 | | |
| $H_2O$ | 45.10 (indirect) | 45.13 | | |
| | 44.28 (ice) | 45.13 | 44.32 | $-R \ln \frac{8}{2}$ |

$R \ln 2$ because it is believed that carbon monoxide can exist in the solid state, with the CO molecules oriented either as CO or OC. Nitrous oxide is another similar example with two possible orientations being NNO or ONN. To obtain agreement between the theoretical and observed entropies of nitric oxide it is assumed that the different orientational configurations in the solid are either

$$\begin{matrix} \text{ON} \\ \text{NO} \end{matrix} \quad \text{or} \quad \begin{matrix} \text{NO} \\ \text{ON} \end{matrix}$$

Per mole of nitric oxide the correction factor is $\frac{1}{2}R \ln 2$. (The entropy of mixing the two forms is $-\frac{1}{4}R \ln \frac{1}{2} - \frac{1}{4}R \ln \frac{1}{2}$ or $\frac{1}{2}R \ln 2$). Note that in all these cases we are dealing with distinguishable configurational differences. Monodeuteromethane has a correction factor of $R \ln 4$ because the deuterium atom can take up four distinguishable configurations in space.

Water offers an especially interesting problem. Pauling[3] suggested that the correction factor for water should be $R \ln 6(\frac{1}{2})^2$ or $R \ln \frac{3}{2}$. The factor 6 arises because there are six distinguishable con-

[3] L. Pauling, *J. Am. Chem. Soc.*, **57**, 2680 (1935).

figurations possible for each molecule in the tetrahedral structure of ice. To understand this, imagine one water molecule at the center of the tetrahedron with four more water molecules, one at each corner of the tetrahedron. Looking at the central water molecule, there are six distinguishable ways in which it can be oriented so that its two hydrogen atoms point toward the four different corners of the tetrahedron, or

$$\frac{4!}{2!2!} = 6$$

Now, in each configuration of the central water molecule, there is a 50–50 chance that the location of each hydrogen atom may be occupied by a hydrogen atom belonging to one of the water molecules on the corners of the tetrahedron. The number 6 has to be multiplied, therefore, by the factor $(\frac{1}{2})^2$.

The statistical thermodynamic entropy[4] calculated for water is 45.13 e.u., which differs from the observed value of 44.28 e.u. found by Giauque and Stout[5] by 0.85 e.u. This is close to the calculated discrepancy of $R \ln \frac{3}{2}$, or 0.806 e.u. predicted by Pauling. Bjerrum[6] does not believe that all of the $(\frac{6}{4})^N$ structures of $N$ water molecules in ice are equally probable because of electrostatic interactions, and states, "consequently it seems necessary to find another explanation of the observed zero-point entropy."

It is interesting to note that if the entropy of water vapor at 25°C is determined experimentally by measuring the entropies of $Mg(OH)_2$, MgO, and the entropy change in the reaction

$$Mg(OH)_2 \rightleftarrows MgO + H_2O$$

the value 45.10 e.u. is found.[7] This value agrees exactly with the spectroscopic value, since in this case there is no possibility of disorder in the crystal similar to that postulated for water.

## 12-3. *The entropy of ethane and other hydrocarbons*

Table 12.3 lists the measured increments in the entropy of ethane[8] from 0 to 298°K.

[4] This value was obtained by W. F. Giauque and R. C. Archibald, *J. Am. Chem. Soc.*, **59,** 561 (1937), who recalculated the data of A. R. Gordon, *J. Chem. Phys.*, **2,** 65 (1934). Gordon had previously obtained 45.10 e.u.

[5] W. F. Giauque and J. W. Stout, *J. Am. Chem. Soc.*, **58,** 1144 (1936).

[6] N. Bjerrum, *Science*, **115,** 385 (1952).

[7] W. F. Giauque and R. C. Archibald, *J. Am. Chem. Soc.*, **59,** 561 (1937).

[8] R. K. Witt and J. D. Kemp, *J. Am. Chem. Soc.*, **59,** 273 (1937); J. D. Kemp and K. S. Pitzer, *J. Am. Chem. Soc.*, **59,** 276 (1937).

The statistical thermodynamic calculation of the entropy of ethane, including the contribution due to the assumed free internal rotation of one methyl group about the other, yields the value 56.36 e.u., which is 1.51 e.u. greater than the observed. This serious discrepancy has been explained on the basis of a potential barrier to rotation of the type already discussed in Secs. 11-3 and 11-4.

TABLE 12.3

THE ENTROPY OF ETHANE

| *Temperature interval or phase change* | *Entropy increment* (e.u.) |
|---|---|
| 0–15°K, Debye function | 0.24 (calculated) |
| 15–89.87° graphical | 10.50 |
| Fusion 682.9/89.87 | 7.60 |
| Liquid 89.87–184.1° graphical | 11.95 |
| Vaporization 3514/184.1 | 19.09 |
| Correction for gas imperfection | 0.16 |
| Gas heating $\int_{184°}^{289°} C_p$ (gas) $d \ln T$ | 5.31 |
| Total entropy | 54.85 ± 0.2 e.u. |

Pitzer and Pitzer and Kilpatrick[9] have calculated thermodynamic functions for a number of straight chain and branched chain hydrocarbons. Table 12.4 lists numerical values of various parameters appearing in the calculation and the observed entropies for the substituted methanes. Calculated entropies were too high, probably due to repulsive forces between methyl groups for which at the present time there is no simple way of correcting theoretically. Pitzer and Pitzer and Gwinn[10] have also developed equations for the calculation of moments of inertia. Pitzer extended his calculations to longer straight chain paraffinic hydrocarbons and to branched chain hydrocarbons by estimating the number of positions in the molecule in which the repulsive energy between methyl groups was $a$ or $2a$, etc., where $a$ was selected to be 800 cal./mole.[11]

[9] K. S. Pitzer, *J. Chem. Phys.*, **8,** 711 (1940); K. S. Pitzer and J. E. Kilpatrick, *J. Chem. Phys.*, **39,** 435 (1946).

[10] K. S. Pitzer, *J. Chem. Phys.*, **5,** 469, 473, 752 (1937); K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10,** 428 (1942).

[11] These positions of higher energy content were determined by the use of wooden molecular models such as those whose model atoms are held together by snap fasteners to allow free rotation as first described by C. E. Black and M. Dole, *J. Chem. Educ.*, **18,** 424 (1941).

TABLE 12.4

NUMERICAL VALUES FOR FREQUENCIES AND OTHER PARAMETERS USED IN THE CALCULATION OF THE ENTROPY OF HYDROCARBONS

| *Substance* | $CH_3CH_3$ | $CH_2(CH_3)_2$ | $CH(CH_3)_3$ | $C(CH_3)_4$ |
|---|---|---|---|---|
| $I_AI_BI_C \times 10^{117}$ g.$^3$ cm.$^6$ | 18.2 | 336 | 1965 | 6570 |
| $I_{int.} \cdot 10^{40}$ g. cm.$^2$ | 2.63 | 4.4 | 5.0 | 5.1 |
| Symmetry number | 6 | 2 | 3 | 12 |
| $V°$ cal./mole | 2800 | 3300 | 3600 | 4700 |
| Skeletal vibration frequencies in cm.$^{-1}$ | 993 | 1053 | 962(2) | 921(3) |
| | | 867 | 794 | 732 |
| | | 373 | 438(2) | 416(3) |
| | | | 370 | 332(2) |
| $CH_3$ Stretching frequencies | | 3000(3) | | |
| $CH_3$ Bending frequencies | | 1400(3) | | |
| | | 1000(2) | | |
| $CH_2$ Stretching frequencies | | 3000(2) | | |
| Bending frequencies | | 1400(2) | | |
| | | 1000(2) | | |
| CH Stretching frequency | | 3000 | | |
| Bending frequency | | 1200(2) | | |
| $S°_{298°}$ (obs) cal./deg., mole | 54.86 | 64.7 | 70.5 | 73.2 |

Classical partition functions were used mostly, including the classical vibrational partition function for the lower frequency vibrations. An effective mass $m$ for each $CH_2$ group amounting to 18.6 atomic weight units was used, but the equations obtained are so complicated and the work so speculative that a detailed description will be omitted. Person and Pimentel[12] have recently brought Pitzer's calculations up to date.

## 12-4. *Corrections to the entropy for nonideal gas behavior*

Up to this point we have been treating all gases as perfect gases without worrying about deviations from the predicted ideal behavior. However, in Tables 12.1 and 12.3 there is listed an item marked "correction for gas imperfection." We shall now describe a method for making these corrections and shall choose as examples methyl and ethyl alcohol, whose corrections are rather large and significant, as calculated recently by Weltner and Pitzer[13] for $CH_3OH$ and Barrow[14] for $C_2H_5OH$. From thermodynamics

[12] W. B. Person and G. C. Pimentel, *J. Am. Chem. Soc.*, **75**, 532 (1953).
[13] W. Weltner, Jr. and K. S. Pitzer, *J. Am. Chem. Soc.*, **73**, 2606 (1951).
[14] G. M. Barrow, *J. Chem. Phys.*, **20**, 1739 (1952).

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{12.4.1}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{12.4.2}$$

or for an ideal gas, the increase in molal entropy as the gas expands at constant temperature from $P_2$ to $P_1$ is

$$S_2 - S_1 = -R \ln \frac{P_2}{P_1} \tag{12.4.3}$$

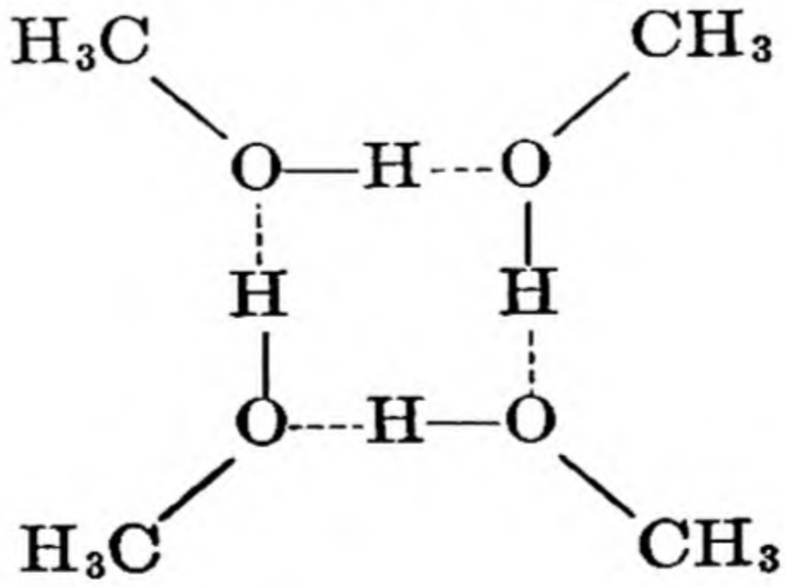
In the case of methyl and ethyl alcohols it is found that the following equation expresses the $PV$ product of the vapor:

$$PV = RT + BP + DP^3 \tag{12.4.4}$$

where $B$ and $D$ are the second and fourth virial coefficients. Equation (12.4.4) yields for the entropy

$$S_2 - S_1 = -R \ln \frac{P_2}{P_1} - (P_2 - P_1)\left(\frac{\partial B}{\partial T}\right)_P - \frac{1}{3}(P_2^3 - P_1^3)\left(\frac{\partial D}{\partial T}\right)_P \tag{12.4.5}$$

The constants $B$ and $D$ result from the tendency of the vapors to form dimers and tetramers, respectively. Thus Weltner and Pitzer[13] postulate that the tetramer is formed because of hydrogen bonding between methyl alcohol molecules in such a way as to produce a symmetrical ring compound as follows:




Equations for $B$ and $D$ are

$$B = b - \frac{RT}{K_2} = b - RTe^{-\Delta S_2/R}e^{\Delta H_2/RT} \tag{12.4.6}$$

$$D = -\frac{3RT}{K_4} = -3RTe^{-\Delta S_4/R}e^{\Delta H_4/RT} \tag{12.4.7}$$

Here $b$ is the co-volume, $K_2$, $K_4$, $\Delta S_2$, $\Delta S_4$, $\Delta H_2$, and $\Delta H_4$ are the pressure equilibrium constants, entropies, and enthalpies of dissociation for the dimer and tetramer, respectively.

The heat capacity of the gas containing small amounts of the dimer and tetramer is given by the equation

$$C_p = C_p^\circ + aP + cP^3 \tag{12.4.8}$$

where

$$a = \frac{\Delta H_2^2}{RT^2} e^{\Delta H_2/RT} e^{-\Delta S_2/R} \tag{12.4.9}$$

and

$$c = \frac{\Delta H_4^2}{RT^2} e^{\Delta H_4/RT} e^{-\Delta S_4/R} \tag{12.4.10}$$

Equations (12.4.9) and (12.4.10) were obtained from the thermodynamic expression

$$C_p - C_p^\circ = -T \int_0^P \left(\frac{\partial^2 V}{\partial T^2}\right)_P dP \tag{12.4.11}$$

or

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{12.4.12}$$

whence

$$\left(\frac{\partial C_p}{\partial P}\right)_T = a + 3P^2 c \tag{12.4.13}$$

$$a = -T \left(\frac{\partial^2 B}{\partial T^2}\right)_P \tag{12.4.14}$$

and

$$c = -\frac{T}{3} \left(\frac{\partial^2 D}{\partial T^2}\right)_P \tag{12.4.15}$$

From the heat capacity data it was possible to find the constants of the above equations as follows:

$\Delta H_2$ (heat of dissociation of the dimer) = 3220 cal./mole
$\Delta H_4$ (heat of dissociation of the tetramer) = 24,200 cal./mole
$\Delta S_2$ = 16.5 e.u.
$\Delta S_4$ = 81.3 e.u.

From the heat of dissociation of the tetramer, the hydrogen bond energy was estimated to be 6050 cal./mole. By correcting for this rather unusual type of gas imperfection, Weltner and Pitzer were able to show that there was no necessity for postulating any residual entropy in the crystals at 0°K. At approximately atmospheric pres-

sure of the vapor of methyl alcohol, the entropy calculated for the ideal gas was 58.63 e.u.; the three correction terms in Eq. (12.4.5) amounted to 0.16, 0.24 and 0.54 e.u., respectively, and the final corrected calculated entropy was 57.69. This agreed well with the observed 57.63 e.u. at 340°K, and illustrates the importance of taking into account the deviation of the behavior of the vapor from that of a perfect gas.

It might be noted that a large change in the heat capacity with pressure at constant temperature indicated the presence of the polymerization phenomenon. For example, at 72.5°C the molal heat capacity decreased from 21.03 to 12.18 cal./mole deg. as the pressure was reduced from 755 to 260 mm. The ideal gas value was calculated to be 11.46 cal./mole deg. At 248.1°C the heat capacity changed only from 14.68 to 14.48 over this pressure range and agreed almost exactly with that calculated for a perfect gas, 14.44 cal./mole deg.

## PROBLEMS

**1.** Calculate the expected difference between the total entropy and the calorimetric entropy for deuterium; also between the total entropy and the spectroscopic entropy.

**2.** Calculate the entropy of propane at 25°C, assuming free rotation, and compare with the observed value given in Table 12.4.

**3.** Prove that in general Eq. (12.1.5) is valid.

# *Chapter 13*

# STATISTICAL THERMODYNAMICS OF ADSORPTION

13-1. Ideal Mobile Monolayer Adsorption. 13-2. Ideal Localized Monolayer Adsorption. 13-3. Ideal Localized Multilayer Adsorption.

## 13-1. *Ideal mobile monolayer adsorption*

Consider a perfect gas, i.e., no interaction between its molecules, constrained to move in a plane. Such a two-dimensional gas would be produced if the gas molecules were adsorbed to the depth of a monolayer, but in such a way that the molecules were free to move over the surface of the adsorbent. Its partition function is easily constructed and we find (for monatomic molecules—no internal degrees of freedom),

$$Q_{M.M.L} = 2\pi mkT\,\frac{\mathcal{A}}{h^2} \tag{13.1.1}$$

where $\mathcal{A}$ is the area available to the monolayer of gas molecules. The Helmholtz free energy is

$$A = -RT \ln\left(\frac{Q_{M.M.L}}{N} + 1\right) \tag{13.1.2}$$

and the spreading tendency (two-dimensional pressure) $X$ follows from the expression

$$\left(\frac{\partial A}{\partial \mathcal{A}}\right)_T = -X \tag{13.1.3}$$

or

$$X\mathcal{A} = RT \tag{13.1.4}$$

which is the equation of state of the ideal mobile monolayer.

## 13-2. *Ideal localized monolayer adsorption*

More interesting, perhaps, than the mobile monolayer is the localized monolayer, since it is this type of adsorption that gives rise to the Langmuir type adsorption isotherm. The assumptions underlying this adsorption model are: (1) no interaction between adsorbed particles, (2) immobility of adsorbed particles on the surface of the adsorbent (i.e., localized adsorption), (3) equilibrium between the adsorbed phase and the gaseous phase, (4) a constant adsorption energy irrespective of extent of surface covered, (5) adsorption to the depth of one layer only.

When $n_1$ molecules are adsorbed on an adsorbent that has $n_s$ adsorption sites, or surface locations that can adsorb one molecule, then in the case of monolayer adsorption, the $n_1$ indistinguishable molecules can be distributed on the $n_s$ distinguishable sites in the following number of distinguishable ways:

$$\frac{n_s!}{(n_s - n_1)!n_1!} \tag{13.2.1}$$

The total partition function $\Phi$ can now be expressed in terms of the individual partition functions of the adsorbed molecule $a_1$ by the equation[1]

$$\Phi = \frac{n_s!}{(n_s - n_1)!n_1!} a_1^{n_1} \tag{13.2.2}$$

The Helmholtz free energy $A$ is

$$A = -kT \ln \Phi \tag{13.2.3}$$

or after approximating the factorials of (13.2.2) by Stirling's approximation,

$$A = -kT\left(n_s \ln \frac{n_s}{n_s - n_1} - n_1 \ln \frac{n_1}{n_s - n_1} + n_1 \ln a_1\right) \tag{13.2.4}$$

The chemical potential per molecule $\mu_1$ of the adsorbed vapor is given by the thermodynamic expression

$$\left(\frac{\partial A}{\partial n_1}\right)_{T,V} = \mu_1 \tag{13.2 5}$$

[1] See R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, London, 1939, p. 426.

but the chemical potential is also related to the partial vapor pressure of the (ideal) gas by the equation

$$\mu = \mu^\circ + kT \ln p \tag{13.2.6}$$

Performing on (13.2.4) the operation indicated by (13.2.5) and equating to (13.2.6), because at equilibrium the chemical potential of the adsorbate must be equal to the chemical potential of the adsorbate in the vapor phase, we obtain

$$\mu = \mu^\circ + kT \ln p = -kT \ln \frac{n_s - n_1}{n_1} - kT \ln a_1 \tag{13.2.7}$$

Now the chemical potential of the vapor in its pure liquid state $\mu^\circ$ is related to its saturated vapor pressure $p^\circ$ and to its partition function in the pure liquid phase $a_L$ by the equation

$$\mu^\circ + kT \ln p^\circ = -kT \ln a_L \tag{13.2.8}$$

Subtracting (13.2.8) from (13.2.7) we find that

$$kT \ln \frac{p}{p^\circ} = -kT \ln \frac{n_s - n_1}{n_1} - kT \ln \left(\frac{a_1}{a_L}\right) \tag{13.2.9}$$

Equation (13.2.9) may be expressed in the equivalent forms, after substituting $c_1$ for $a_1/a_L$, and $x$ for $p/p_0$

$$x = \frac{n_1}{n_s - n_1} \cdot \frac{1}{c_1} \tag{13.2.10}$$

and

$$\frac{n_1}{n_s} = \frac{c_1 x}{1 + c_1 x} \tag{13.2.11}$$

Equation (13.2.11) is the well-known Langmuir adsorption isotherm, which has here been derived on the basis of an equilibrium, statistical thermodynamic point of view. We shall defer discussing the significance of the constant $c_1$ until equations for multilayer adsorption have been developed.

## 13-3. *Ideal localized multilayer adsorption*

The statistical thermodynamics of the extension of the Langmuir adsorption isotherm has been developed by Cassie,[2] Hill,[3] and Dole.[4] The assumptions underlying this treatment are much the same as

[2] A. B. D. Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).
[3] T. E. Hill, *J. Chem. Phys.*, **14**, 263 (1946).
[4] M. Dole, *J. Chem. Phys.*, **16**, 25 (1948).

those employed above in the derivation of the Langmuir equation; new assumptions are that molecules can become adsorbed on top of each other, so that adsorption to the depth of many layers can occur. Equilibrium between each layer and between the top layer and the vapor phase is assumed. Although particles can interact with those above and below them (vertical interaction), the assumption is made that there is no interaction between particles adsorbed in the same layer (horizontal interaction). The total number $n$ of adsorbed molecules is given by the equation

$$n = n_1 + n_2 + n_3 + \ . \ . \ . \ + n_n$$

where the subscripts indicate the number of the layer, e.g., the first, second, or third layer, etc.

For each of the

$$\frac{n_s}{(n_s - n_1)!n_1!}$$

ways that $n_1$ molecules can be adsorbed on $n_s$ sites, there are

$$\frac{n_1!}{(n_1 - n_2)!n_2!}$$

ways that $n_2$ molecules can be adsorbed on the $n_1$ molecules in the first layer to make the second layer. The total partition function for multilayer adsorption can therefore be written

$$\Phi = \frac{n_s!}{(n_s - n_1)!n_1!} \cdot \frac{n_1!}{(n_1 - n_2)!n_2!} \cdot \frac{n_2!}{(n_2 - n_3)!n_3!} \ . \ . \ . \ a_1^{n_1} a_2^{n_2} a_3^{n_3} \ . \ . \ . \qquad (13.3.1)$$

Taking logarithms of (13.3.1) and applying the usual Stirling approximation,

$$\ln \Phi = n_s \ln \frac{n_s}{n_s - n_1} + n_1 \ln \frac{n_s - n_1}{n_1 - n_2} + n_2 \ln \frac{n_1 - n_2}{n_2 - n_3} + \ . \ . \ . + n_1 \ln a_1 + n_2 \ln a_2 + \ . \ . \ . \qquad (13.3.2)$$

For equilibrium between the first and second layers of adsorbed molecules, we imagine an infinitesimal change in the number of particles in the first and second layers such that

$$dn_1 = -dn_2; \qquad dn_3 = dn_4 = dn_5 = \ . \ . \ . \ = 0$$

and

$$\left(\frac{\partial \ln \Phi}{\partial n_1}\right)_{T,V,n_3,n_4,\ldots} = 0 \qquad (13.3.3)$$

(At equilibrium the free energy of the adsorption system should not be altered by transfer of an infinitesimal number of molecules from the first to the second layer.) Differentiating (13.3.2) with respect to $n_1$ and remembering that $dn_1$ equals $-dn_2$, we obtain the interesting result,

$$\frac{n_s - n_1}{n_1 - n_2} = \frac{n_1 - n_2}{n_2 - n_3} \cdot \frac{a_2}{a_1} \tag{13.3.4}$$

It can also be shown for equilibrium between the second and third layers that

$$\frac{n_1 - n_2}{n_2 - n_3} = \frac{n_2 - n_3}{n_3 - n_4} \cdot \frac{a_3}{a_2} \tag{13.3.5}$$

and in general

$$\frac{n_i - n_{i+1}}{n_{i+1} - n_{i+2}} = \frac{n_{i+1} - n_{i+2}}{n_{i+2} - n_{i+3}} \cdot \frac{a_{i+2}}{a_{i+1}} \tag{13.3.6}$$

The relationship expressed by (13.3.6) illustrates an interesting feature of multilayer adsorption based on the model adopted here;

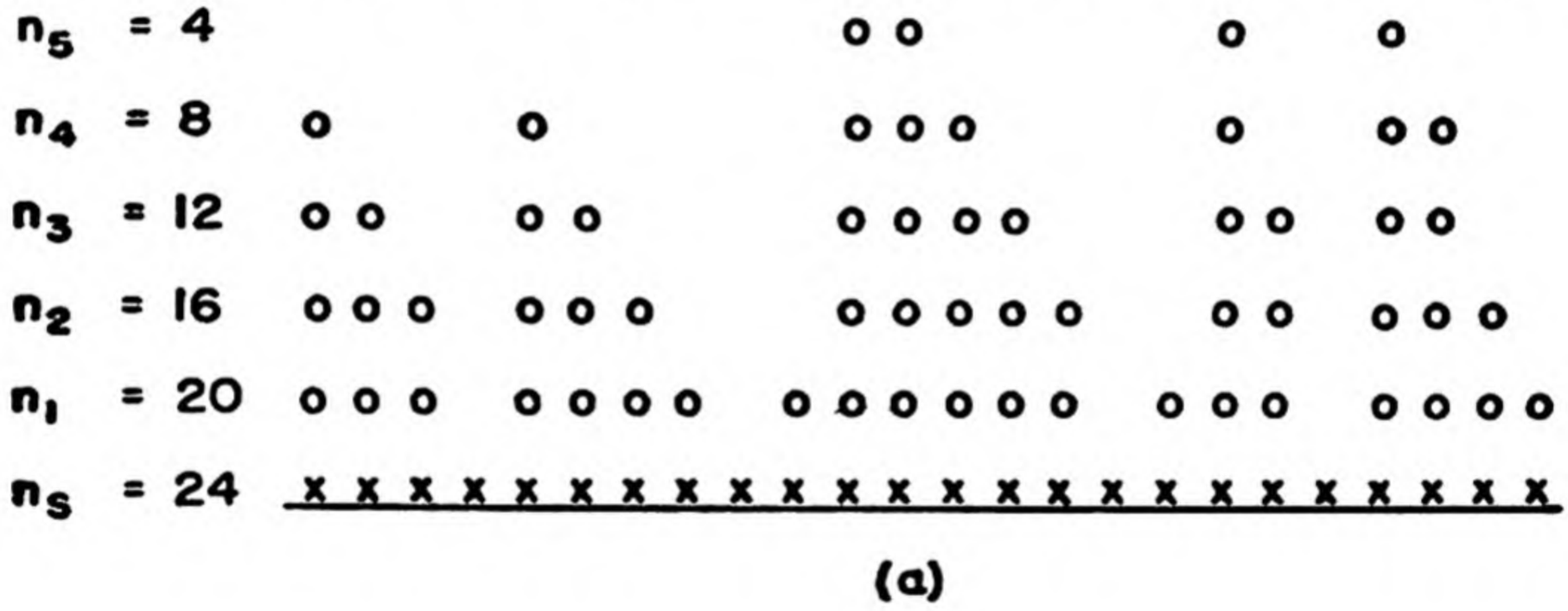



**Fig. 13.1.** (a). Multilayer adsorption. (b) The B.E.T. model.

namely, a pyramidal type of adsorption in which the number of molecules in each succeeding layer is always less than the layer immediately below it. In Fig. 13.1 (a) this statement is illustrated

for the case that $a_{i+1} = a_i$, and in Fig. 13.1 (b) for the case that $a_2 = 0.5a_1$, $a_3 = a_4 = \cdot\ \cdot\ \cdot$ . (We would expect $a_{i+1}$ to be smaller, in general, than $a_i$, but the ratio to approach unity as $i$ increases, as explained below.)

Continuing now with the mathematical development, the relationship that expresses the equilibrium between the top adsorbed layer (designated by the subscript $n$) and the gas phase is

$$-kT\left(\frac{\partial \ln \Phi}{\partial n_n}\right)_{T,V} = \mu = \mu^\circ + kT \ln p \qquad (13.3.7)$$

From Eq. (13.3.8)

$$\frac{n_{n-2} - n_{n-1}}{n_{n-1} - n_n} = \frac{n_{n-1} - n_n}{n_n} \cdot \frac{a_n}{a_{n-1}} \qquad (13.3.8)$$

which follows from (13.3.6);

$$kT \ln \frac{n_n}{n_{n-1} - n_n} - kT \ln a_n = \mu = \mu^\circ + kT \ln p \qquad (13.3.9)$$

which follows from (13.3.7); and

$$-kT \ln a_L = \mu^\circ + kT \ln p_0 \qquad (13.2.8)$$

as given in the previous section, it is possible to show that

$$\frac{n_n}{n_{n-1} - n_n} = xc_n \qquad (13.3.10)$$

Now if the value of $(n_1 - n_2)/(n_2 - n_3)$ in Eq. (13.3.4) is replaced by its value in Eq. (13.3.5), and $(n_2 - n_3)/(n_3 - n_4)$ is replaced by

$$\frac{n_3 - n_4}{n_4 - n_5} \cdot \frac{a_4}{a_3}$$

and so on, we finally reduce (13.3.4) to

$$(n_1 - n_2) = (n_s - n_1)xc_1 \qquad (13.3.11)$$

where

$$c_1 = \frac{a_1}{a_L}$$

Similarly, it follows that

$$\begin{aligned} n_2 - n_3 &= (n_s - n_1)x^2c_1c_2 \\ n_3 - n_4 &= (n_s - n_1)x^3c_1c_2c_3 \\ &\cdots\cdots\cdots\cdots\cdots \\ n_n &= (n_s - n_1)x^nc_1 \ \ldots\ c_n \end{aligned} \qquad (13.3.12)$$

The purpose of this treatment is to obtain an equation explicitly relating $n$, the total number of molecules adsorbed in all layers, to the relative vapor pressure $x$. The total number of molecules adsorbed can be expressed by the identity

$$n \equiv (n_1 - n_2) + 2(n_2 - n_3) + 3(n_3 - n_4) + \ . \ . \ . \qquad (13.3.13)$$

or substituting (13.3.11) and (13.3.12) into (13.3.13), we obtain

$$n = (n_s - n_1)xc_1 + 2(n_s - n_1)x^2c_1c_2 + \ . \ . \ . \qquad (13.3.14)$$

or

$$n = (n_s - n_1)xc_1(1 + 2xc_2 + 3x^2c_2c_3 + \ . \ . \ .)$$

We also have the identity

$$n_s \equiv (n_s - n_1) + (n_1 - n_2) + (n_2 - n_3) + \ . \ . \ .$$

or on substituting from (13.3.11) and (13.3.12),

$$n_s = (n_s - n_1)(1 + xc_1 + x^2c_1c_2 + \ . \ . \ .) \qquad (13.3.15)$$

Dividing (13.3.14) by (13.3.15) we obtain,[5]

$$\frac{n}{n_s} = \frac{xc_1(1 + 2xc_2 + 3x^2c_2c_3 + \ . \ . \ .)}{1 + xc_1 + x^2c_1c_2 + \ . \ . \ .} \qquad (13.3.16)$$

Now the numerator of (13.3.16) is seen to be the derivative of the denominator with respect to $x$, after multiplication by $x$; hence if we let

$$\varphi = 1 + xc_1 + x^2c_1c_2 + \ . \ . \ .$$

and

$$\frac{d\varphi}{dx} = \varphi' = c_1 + 2x_1c_1c_2 + \ . \ . \ .$$

$$= c_1(1 + 2xc_2 + 3x^2c_2c_3 + \ . \ . \ .)$$

Eq. (13.3.16) can be simplified to

$$\frac{n}{n_s} = \frac{x\varphi'}{\varphi} \qquad (13.3.17)$$

To proceed further with (13.3.17) we have to make some assumptions concerning the partition function ratios, $c_1$, $c_2$, etc. As the

[5] It is interesting to note that Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918) included in his adsorption theory a solution of the multilayer case by a kinetic approach and arrived at an equation equivalent to (13.3.16).

adsorption proceeds, it is reasonable to suppose that the adsorbed molecules become more and more equivalent to molecules in the liquid state with respect to the zero of energy, rotations, oscillations, and vibrations. We might expect, therefore, the internal partition function ratio, which is constant at constant temperature, to approach unity as the amount of adsorbed material per unit of adsorbent becomes greater and greater.

One limiting case would have the constant $c$ equal to unity for all adsorbed layers. Such a case could be represented by the adsorption of toluene by benzene, if we can speak of the dissolving of toluene by benzene as an adsorption. One can, perhaps, conceive of each benzene molecule as an "adsorption site" for toluene molecules. In fact, in the statistical thermodynamic treatment given here we have made no statements that are restricted to adsorption *onto* a surface. Sorption *within* a material is permissible as long as equilibrium exists between the sorbate and its vapor. If the sorbent swells, one would have to consider an entropy of swelling, but in the benzene-toluene system, there is no net change of volume on mixing, no heat of mixing, at least to a first very close approximation, so that we can consider the mixture of the two to be an ideal solution with the internal partition function of the toluene unchanged on being mixed with the benzene. If we consider, then, the net process

$$\text{toluene (liquid)} + \text{benzene (liquid)} \rightarrow \text{solution of toluene in benzene}$$

we can apply Eq. (13.3.17) and take all the $c$ constants as being equal to unity. We also postulate an infinite number of adsorption layers. With these stipulations, $\varphi$, our function of $x$, becomes

$$\varphi = \frac{1}{1-x}; \qquad \varphi' = \frac{1}{(1-x)^2}$$

and

$$\frac{n}{n_s} = \frac{x}{1-x} \tag{13.3.18}$$

Solving for $x$,

$$x = \frac{n}{n+n_s} \tag{13.3.19}$$

If we let $n_s$ represent the number of benzene molecules, then $n/(n+n_s)$ is the mole fraction of toluene, and

$$x = \text{N} \tag{13.3.20}$$

which is Raoult's law for the vapor pressure of a volatile component of a solution as a function of its mole fraction.

The next case of interest to us is one in which all $c$ constants beyond the first layer are taken equal to unity. This assumption is based on the idea that by far the greatest change in the partition function of the liquid molecule occurs when the molecule is adsorbed onto the bare adsorbent, and is the fundamental concept adopted by Brunauer, Emmett, and Teller[6] in their kinetic derivation of the B.E.T. adsorption equation. Letting

$$c_2 = c_3 = c_4 = \ . \ . \ . \ = 1$$

we find for $\varphi$ and $\varphi'$

$$\varphi = 1 + xc_1(1 + x + x^2 + \ . \ . \ .) = 1 + \frac{xc_1}{1 - x}$$

$$\varphi' = \frac{c_1}{(1 - x)^2}$$

and

$$\frac{n}{n_s} = \frac{xc_1}{(1 - x)(1 - x + xc_1)} \tag{13.3.21}$$

which is the well-known B.E.T. adsorption isotherm.

Another interesting case, which may, however, be without physical significance, is that in which the $c$ constants decrease harmonically as the number of layers increases, i.e.,

$$c_2 = \tfrac{1}{2}c_1; \qquad c_3 = \tfrac{1}{3}c_1; \qquad \text{etc.}$$

Under this assumption it is readily shown that

$$\varphi = 1 + c_1x + \frac{c_1^2x^2}{1 \cdot 2} + \frac{c_1^3x^3}{1 \cdot 2 \cdot 3} + \frac{c_1^4x^4}{4!} + \ . \ . \ .$$

$$\varphi = e^{c_1x}; \qquad \varphi' = c_1e^{c_1x}$$

and

$$\frac{n}{n_s} = c_1x \tag{13.3.22}$$

which is a linear adsorption isotherm.

At this point we should investigate the $c$ parameters that we have used in the above equations. If the partition function representing all the degrees of internal freedom including vibrations and rotation

[6] S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

of the adsorbed molecule is known, as well as the contribution due to vibrations normal to the surface, we can designate this function $j(T)$. Multiplying this partition function by the partition function factor defining the zero of energy, we obtain $a_1$, the partition function of one molecule in the first adsorbed layer. The energy of the lowest or zero level in the adsorbed state is equal to the negative of the difference between the energy of the molecules in a vacuum an infinite distance apart and the energy of the molecule adsorbed onto the adsorbent in the first layer. This zero level energy in the adsorbed state is called the adsorption energy. If the adsorbed molecules interact with each other, an expression involving the potential energy of such interactions would have to be included in $a_1$. We express $a_1$ for the purposes of the adsorption theory given here by

$$a_1 = j(T)e^{-\epsilon^\circ_1/kT} \tag{13.3.23}$$

where $\epsilon_1^\circ$ is the energy of the adsorbed molecule in the first layer at the absolute zero of temperature. Since $\epsilon_1^\circ$ is always negative, the exponential factor of (13.3.23) will always be greater than unity. To obtain $c_1$, we divide $a_1$ by $a_L$, the partition function of the adsorbed material in the pure liquid state. The problem of obtaining valid liquid state partition functions is very great, but progress has been made on the basis of models approximating the liquid state. If one assumes that molecules are vibrating about a position of minimum potential energy with frequency $\nu$ and energy $\epsilon_L^\circ$ we obtain the harmonic oscillator model partition function of the liquid,[7]

$$\Omega(T) = \left\{\left(\frac{kT}{2\pi m\nu^2}\right)^{3/2} e^{-\beta(\epsilon^\circ_L - kT)}\right\}^N \tag{13.3.24}$$

where the function $\Omega$ has the dimensions of $V^N$.

The ratio of $a_1$ to $a_L$ will contain a number of constant quantities at constant temperature multiplied by the factor

$$e^{-\beta(\epsilon^\circ_1 - \epsilon^\circ_L)} \tag{13.3.25}$$

where $\epsilon_1^\circ - \epsilon_L^\circ$ is roughly the difference between the heat of adsorption and the heat of condensation. However, if $\epsilon_1^\circ - \epsilon_L^\circ$ is calculated from $c_1$, neglecting all other factors, the result does not agree at all well with the heat of adsorption less the heat of condensation as calculated from the variation of the adsorption with the tempera-

[7] See Fowler and Guggenheim, *op. cit.*, p. 325.

ture. This indicates that the other factors in $a_1$ and $a_L$ besides $\epsilon_1^\circ$ and $\epsilon_L^\circ$ have to be considered.

We conclude this chapter with a few references to recent theoretical studies of adsorption. Thus Halsey[8] proves that the B.E.T. theory is invalid if the adsorption of one molecule in the second layer requires at least a triangular array of molecules in the first layer to serve as an adsorption site. He does not believe that a molecule in the second layer can be adsorbed on top of a single molecule in the first layer. He shows how "horizontal" interaction, interaction between molecules adsorbed in the same layer, can lead to stepwise adsorption isotherms. This had also been pointed out by Dole.[4]

Earlier, Halsey and Taylor, and Sips had demonstrated that a distribution of adsorption energies over the surface can lead to a Freundlich type adsorption isotherm.[9] "Vertical" interaction, i.e., interaction between molecules in different adsorbed layers or between the adsorbent and adsorbed molecules beyond the first layer, is supposed to be responsible for multilayer adsorption.

McMillan[10] suggests that a better fit of the data to the B.E.T. equation at low values of $x$ is obtained if two or more $c$ values are used. This is equivalent to assuming surface heterogeneity. In another and more recent paper McMillan and Teller[11] consider the influence of surface tension forces on multilayer adsorption. Their conclusion is that the surface tension effect overcorrects the B.E.T. theory.

Reference should also be made to the many important papers by Hill[12] on the statistical thermodynamics of adsorption, but the discussion of these is beyond the scope of this book.

## PROBLEMS

1. Derive Eq. (13.1.1).
2. What is the heat capacity of the ideal mobile adsorbed monolayer?

[8] G. Halsey, *J. Chem. Phys.*, **16,** 931 (1948); *J. Am. Chem. Soc.*, **73,** 2693 (1951); **74,** 1082 (1952).
[9] G. Halsey and H. S. Taylor, *J. Chem. Phys.*, **15,** 624 (1947); R. Sips, *J. Chem. Phys.*, **16,** 490 (1948).
[10] W. G. McMillan, *J. Chem. Phys.*, **15,** 390 (1947).
[11] W. G. McMillan and E. Teller, *J. Chem. Phys.*, **19,** 25 (1951).
[12] T. L. Hill, *J. Chem. Phys.*, **19,** 261 (1951); **16,** 181 (1948); **15,** 767 (1947); **14,** 263, 441 (1946); and others.

**3.** Imagine the water molecule adsorbed on a solid in such a way that the molecule has no translational degrees of freedom, only one rotational degree of freedom (about the axis that bisects the HOH angle), but its usual vibrational degrees of freedom. Neglecting the contribution due to interaction of the water molecule with the solid, develop an equation for its partition function.

**4.** Solve Eq. (13.3.17) for the case that

$$c_1 \neq c_2 = c_3 = c_4 = \ . \ . \ . \ ; \quad c_2 \neq 1.$$

**5.** Obtain an explicit expression for $n_1/n_s$ for the B.E.T. model.

**6.** Prove that for multilayer adsorption in the B.E.T. case

$$\left(\frac{n}{n_s}\right)_{c=\infty} = \left(\frac{n}{n_s}\right)_{c=1} + 1$$

at any value $x$ of the relative pressure.

**7.** Prove for multilayer adsorption and for all $c$'s equal to unity that the fraction of the surface covered in the first layer is always equal to $x$.

# *Chapter 14*

# BOSE-EINSTEIN AND FERMI-DIRAC STATISTICS

14-1. Introduction. 14-2. The Bose-Einstein Statistics. 14-3. The Fermi-Dirac Statistics.

## 14-1. *Introduction*

Although this book deals essentially with the subject of statistical thermodynamics, we feel that before concluding it, statistical systems known as the Bose-Einstein and Fermi-Dirac statistics should be briefly described. One of the fundamental principles of nature seems to be that all elementary particles and all nuclei of odd mass number or particles with half integral spin follow in their behavior the requirements of the Fermi-Dirac Statistics, while nuclei of even mass number and photons or particles of zero or integral spin follow the Bose-Einstein statistics. For atoms the number of extranuclear electrons must also be counted. Fowler and Guggenheim[1] state that when the assembly eigenfunctions are symmetrical in all the systems of a given set, the assemblies of such systems are said to obey the Bose-Einstein statistics. When the assembly eigenfunctions are antisymmetrical in all the systems of a given set, the assemblies of such systems are said to obey the Fermi-Dirac statistics.

As a matter of fact, as we shall see, it is only when the density of the particles concerned is high that we need to invoke either of these newer statistics to replace classical or Boltzmann statistics. Examples are helium in the neighborhood of the absolute zero where helium isotope of mass 4, presumably obeying the laws based on Bose-Einstein statistics, has markedly different physical properties

[1] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, London, 1939, p. 45.

from helium isotope of mass 3, presumably following the laws of the Fermi-Dirac statistics.[2] The conduction electrons in metals have the properties of a Fermi-Dirac gas, while the radiation laws can be derived from application of the Bose-Einstein statistics to an assembly of photons. The Boltzmann distribution law and all classical statistics follow from either the Bose-Einstein or Fermi-Dirac statistics when the density of the particles is not high.

## 14-2. *The Bose-Einstein statistics*

In Chapter 4 we considered the distribution of molecules among a number of energy states, with the understanding that the molecules were tagged so that an interchange of two molecules produced a new complexion. Actually, molecules are indistinguishable, so that we counted too many complexions, and although this error had no effect on the Boltzmann distribution law, on the total energy, or heat capacity, it did influence the entropy, requiring subtraction of the term $k \ln n!$ from the entropy when a mixture or assembly of molecules was considered. We could have justified the treatment of Chapter 4 by identifying the energy states and the position of the energy states in space as in a crystal. The counting method used in Chapter 4 could have been applied to distribution of the particles among localized energy states such as the vibrational energy states of atoms in a solid. Then an interchange of two identical particles between two energy states (but without change of location of either particle) would have produced a distinguishable change in the distribution; however, as we wished to develop equations applicable to perfect gases, we did not wish to avoid the necessity of subtracting $k \ln n!$ from the entropy.

In the Bose-Einstein statistics it is unnecessary to assume the distinguishability of the particles; from the outset identical particles are considered to be indistinguishable, and the number of complexions counted accordingly. Thus in Fig. 4.1 there are 10 distinguishable configurations illustrated, provided that the particles are labeled. When the physical indistinguishability of the particles is recognized, the number of complexions drops to three.

Let us consider the distribution of particles among the available energy states of a gas. First of all, it must be realized that there are at normal temperatures and pressures vastly more energy states avail-

[2] B. M. Abraham, D. W. Osborne, and B. Weinstock, *Science*, **117**, 121 (1953).

able than there are molecules. From Eq. (4.2.3) the average translational energy of a molecule increases by $2 \times 10^{-16}$ erg when the temperature increases by 1°C, yet from Eq. (4.2.1) we calculate that the increase of $k_x$ by one unit increases the energy by only $9.2 \times 10^{-23}$ erg (at 300°K). The total number of energy states is equal to one-eighth the volume of a sphere of radius $r$, where

$$r^2 = k_x^2 + k_y^2 + k_z^2 \tag{14.2.1}$$

At 300°K, $r$ is of the order $10^8$ and the number of energy states is of the order $10^{24}$. This is for a 1 cm. cube, which at normal pressures would contain only about $10^{19}$ molecules.

Let us now select a range of energy small in comparison to $kT$ but large enough to contain enough particles so that Stirling's approximation can be used. Let the range of energy be small so that all the particles having energies within this range may be considered to have the same energy. The number of quantum states within this range will also be large. The number of ways in which $n_s$ indistinguishable particles may be distributed among $C_s$ quantum states with no limitation on the number per state is given by the expression

$$\frac{(C_s + n_s - 1)!}{(C_s - 1)!n_s!} \tag{14.2.2}$$

Equation (14.2.2) can be understood by first considering the number of ways in which $n_s$ particles plus the number, $C_s - 1$, of partitions between $C_s$ compartments can be permuted; this is the numerator of (14.2.2). Second, by dividing this number by the number of ways $n_s$ particles can be permuted among themselves and by the number of ways $C_s - 1$ partitions between the $C_s$ compartments can be permuted among themselves, the denominator of (14.2.2) is obtained. The total number of distinguishable complexions is obtained from (14.2.2) by taking the product of expressions like (14.2.2) over all the $s$ energy ranges. This product will be equal to the thermodynamic probability of the distribution of the energy among the particles, or

$$W_t = \prod_s \frac{(C_s + n_s - 1)!}{(C_s - 1!)n_s!} \tag{14.2.3}$$

Proceeding as in Chapters 4 and 5, take logarithms of (14.2.3), apply the Stirling approximation, and take the variation of ln $W_t$ to find the condition for the maximum probability. The equation

$$\sum_s \ln \frac{(C_s + n_s - 1)}{n_s} \delta n_s = 0 \qquad (14.2.4)$$

is obtained. At this point it is convenient to neglect unity in comparison to the sum of $C_s$ and $n_s$, so that (14.2.4) simplifies to

$$\sum_s \ln \left(1 + \frac{C_s}{n_s}\right) \delta n_s = 0 \qquad (14.2.5)$$

The conditions for constant total energy and constant total number of particles are now introduced:

$$\sum_s \beta \epsilon_s \, \delta n_s = 0 \qquad (14.2.6)$$

$$\sum_s \alpha \, \delta n_s = 0 \qquad (14.2.7)$$

Subtracting (14.2.6) and (14.2.7) from (14.2.5) and solving by the Lagrangian method of undetermined multipliers, the Bose-Einstein distribution law results:

$$\frac{n_s}{C_s} = \frac{1}{e^{\alpha} e^{\beta \epsilon_s} - 1} \qquad (14.2.8)$$

At this point it should be noted that if unity is neglected in the denominator of Eq. (14.2.8), the Boltzmann distribution law is obtained [compare Eq. (5.1.8)].

$$n_s = C_s e^{-\alpha} e^{-\beta \epsilon_s} \qquad (14.2.9)$$

The term $e^{\alpha}$ was shown to be related to the partition function by the equation

$$e^{\alpha} = \frac{Q}{N}$$

or for a perfect gas whose translational free energy can be reduced to the equation

$$F = -RT \ln \frac{Q}{N} \qquad (9.2.2)$$

$$\alpha = -\frac{F}{RT} \qquad (14.2.10)^{3}$$

[3] Equation (14.2.10) is valid for a one-component system; otherwise the numerator of (14.2.10) should contain the chemical potential $\mu$ instead of the free energy $F$.

At 0°C and 1 atmosphere pressure the molal entropy of argon, assumed to be a perfect gas, is 36.5 e.u., which gives for the value of $F/RT$ approximately $-15.7$. The quantity $e^{\alpha}$ then takes the value $6.6 \times 10^6$, which is vastly greater than unity and justifies our neglect of unity in the denominator of (14.2.8). However, considering translational energies,

$$e^{\alpha} = \frac{Q}{N} = \frac{(2\pi mkT)^{3/2}}{h^3}\frac{V}{N} \tag{14.2.11}$$

$e^{\alpha}$ would have its smallest value for gases of the smallest mass and at the lowest temperatures at which gases can exist. Thus at the boiling point[4] of $He^4$, 4.2°K and 1 atmosphere pressure, $e^{\alpha}$ equals 7.5.

The lighter isotope of helium, $He^3$, boils[2] at 3.20°K. For this substance, $e^{\alpha}$ equals 4.95 [assuming its nuclear spin to be one-half and including a nuclear spin weight of 2 in (14.2.11)]. However, $He^3$ would be expected to follow Fermi-Dirac statistics because of the odd number of particles in its nucleus. The value of 7.5 is low enough so that at very low temperatures deviations in the behavior of $He^4$ from the predictions of the Boltzmann statistics might be observable. In condensation phenomena, van der Waals intermolecular forces also play a part, and it is difficult to separate the effect of the statistics from that of the intermolecular forces. Nevertheless, $He^3$ exhibits no superfluidity, at least down to 1°K; consequently, it probably exhibits no lambda point transition similar to that of $He^4$. Thus the marked differences between $He^4$ and $He^3$ are undoubtedly due to the fact that these two substances follow different statistics.

Considering the fact that in the Bose-Einstein statistics there is no limit to the number of particles in each energy state, we might expect the Bose-Einstein gas to condense to a liquid more readily in the case of $He^4$ than $He^3$. This indeed turns out to be the case as can be seen from the data[2] of Table 14.1, where the vapor pressures of $He^4$ and $He^3$ and their ratio are listed as a function of temperature in the neighborhood of the absolute zero.

At 2.19°K, $He^4$ undergoes a peculiar condensation or transition in which its physical and thermodynamic properties change abruptly. At this temperature, called the $\lambda$ point, the specific heat rises to a

[4] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, Inc., New York, 1940, p. 121.

TABLE 14.1

VAPOR PRESSURES OF $He^4$ AND $He^3$

| $T$ (°K) | $p_{He^3}$ (mm. Hg) | $p_{He^4}$ (mm. Hg) | $p_{He^3}/p_{He^4}$ |
|---|---|---|---|
| 1.0 | 8.7 | 0.12 | 72 |
| 1.5 | 50.7 | 3.59 | 14 |
| 2.0 | 152 | 24.2 | 6.3 |
| 2.5 | 334 | 78.5 | 4.3 |
| 3.0 | 618 | 183 | 3.4 |
| 3.35 | 890 | 293 | 3.0 |

sharp maximum, and below it liquid helium becomes superfluid and its thermal conductance increases enormously. London[5] explained in part the transition by postulating a condensation of atoms in momentum space. Einstein[6] had earlier mentioned the possibility of such a phenomenon. What this means is that some of the atoms at this very low temperature have fallen in energy down to their lowest or zero energy level. Their gas kinetic energy has been reduced practically to zero. This does not mean that two phases exist, merely that the liquid helium consists of some atoms whose momentum is the lowest possible value and that do not contribute to the pressure, and some that still possess exchangeable momentum. All the atoms, when vibrating in the liquid phase, will have the usual zero point energy and will contribute to the density of the liquid.

Band[7] concludes from an application of Bose-Einstein statistics to adsorption phenomena that $He^4$ should show a rapid increase in adsorption at a critical temperature. As such a critical adsorption phenomenon would not be expected for $He^3$, which is possibly adsorbed only in a first localized monolayer, all mobile monolayers beyond the first should be practically pure $He^4$.

## 14-3. *The Fermi-Dirac statistics*

While in the case of the Bose-Einstein statistics there was no restriction on the number of particles contained in each small region of energy, in the Fermi-Dirac statistics the Pauli exclusion principle applies, and only one particle per energy state is permitted. The number of distinguishable ways in which $n_s$ indistinguishable

[5] F. London, *Phys. Rev.*, **54,** 947 (1938); *J. Phys. Chem.*, **43,** 49 (1939).
[6] A. Einstein, *Ber. Berlin Akad.*, 261 (1924); 3 (1925).
[7] W. Band, *J. Chem. Phys.*, **19,** 435 (1951).

particles may be distributed among $C_s$ distinguishable energy states with not more than one particle per state is given by

$$\frac{C_s!}{(C_s - n_s)!n_s!} \qquad (14.3.1)'$$

Equation (14.3.1) is also equal to the number of distinguishable ways in which $n_s$ molecules can be adsorbed onto $C_s$ adsorption sites, Eq. (13.2.1). The validity of (14.3.1) can be appreciated by considering that it represents the number of complexions or the number of ways in which $(C_s - n_s)$ empty sites can be selected from a total of $C_s$ sites. Equation (14.3.1) is entirely equivalent to (2.3.4) whose derivation has already been given in Chapter 2.

We proceed mathematically exactly as in the preceding section, arriving finally at the Fermi-Dirac distribution law:

$$n_s = \frac{C_s}{e^{\alpha}e^{\beta\epsilon} + 1} \qquad (14.3.2)$$

We have seen above that $\alpha = -\mu/kT$, where $\mu$ is the chemical potential per molecule or the partial free energy per molecule. We can write (14.3.2) in the form, therefore

$$n_s = \frac{C_s}{e^{(\epsilon - \mu)/kT} + 1} \qquad (14.3.3)$$

The Fermi-Dirac statistics are particularly applicable to metals, whose properties are explained on the hypothesis that one or more of the valence electrons per atom are substantially free to move around within the metal in a field-free space (actually there will be a small periodic field that may be neglected to a first approximation). We can apply to these conduction electrons the wave equation for a particle in a box and obtain the energy states given by Eq. (9.1.9) as the allowed energy states for the conduction electrons in a metal.

The electron gas in the metal does not, of course, condense at the absolute zero of temperature; the electrons do, however, seek the lowest allowed energy states. But only two electrons are allowed to occupy each energy state (two because of the two possible directions of the electron spin). Thus the energy states will fill up until all the electrons have been accommodated. Following Mayer and Mayer,[8] let us designate the energy of the uppermost filled level by the

[8] Mayer and Mayer, *op. cit.*, p. 375.

symbol $\mu^\circ$. The value of this energy is easily found by equating the total number of electrons to the number of energy states whose energy is equal to or less than $\mu^\circ$. From Eq. (9.1.9) it is clear that the number of energy states is equal to the volume of one-eighth of the sphere of radius $r$, where $r^2$ is equal to $k_x^2 + k_y^2 + k_z^2$ (compare the similar method used in counting the allowed frequencies of vibration within a solid, Chapter 10). Remembering that each energy state will have a twofold degeneracy due to the electron spin, we obtain the equation for $\mu^\circ$,

$$\mu^\circ = \frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{2/3} \tag{14.3.4}$$

Considering potassium, whose valence electron density $n/V$ in solid potassium is $1.32 \times 10^{22}$ electrons per cubic centimeter, $\mu^\circ$ is readily calculated to be $3.25 \times 10^{-12}$ erg/electron, or $4.68 \times 10^4$ cal./mole of electrons. Thus the electrons in the highest energy states at the absolute zero of temperature have energies equivalent to a kinetic theory temperature of about 15,000°K.

Referring now to Eq. (14.3.3), we can see that at the absolute zero, the exponential term of the denominator will be equal to either infinity or zero, depending on whether $\epsilon_s$ is greater or less than $\mu^\circ$. As a consequence, the distribution of electrons has the form of the solid line shown in Fig. 14.1. When the temperature rises, a few electrons will acquire enough energy so that some of the energy states above $\mu^\circ$ will become populated, but relatively speaking the number of such promoted electrons is few. (Only about the top 10% of the energy range is illustrated in Fig. 14.1.) This accounts for the fact that the kinetic motion of the electrons makes a negligible contribution to the specific heats of solid metals, and explains why Einstein and Debye in developing their theories of the specific heats of solids ignored the conduction electrons.

It is interesting to calculate the pressure of the electron gas, which by thermodynamics is given by

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \tag{14.3.5}$$

Now, the entropy of the electron gas is zero at the absolute zero, since all energy levels are full up to $\mu^\circ$ and essentially only one configuration is possible (except for a possible small degeneracy in the

uppermost energy level). Hence the Helmholtz free energy $A$ is equal to the energy $E$, and as the average energy per electron is $\frac{3}{5}\mu^\circ$ (see problem 2, Sec. 14-4),

$$A^\circ = E^\circ = N\frac{3h^2}{40m}\left(\frac{3n}{\pi V}\right)^{2/3} \tag{14.3.6}$$

and

$$P = \frac{N}{20V}\cdot\frac{h^2}{m}\left(\frac{3n}{\pi V}\right)^{2/3} \tag{14.3.7}$$

For potassium, Eq. (14.3.7) gives a pressure of 5700 atmospheres! Despite this high internal pressure of the electrons, the electrons can

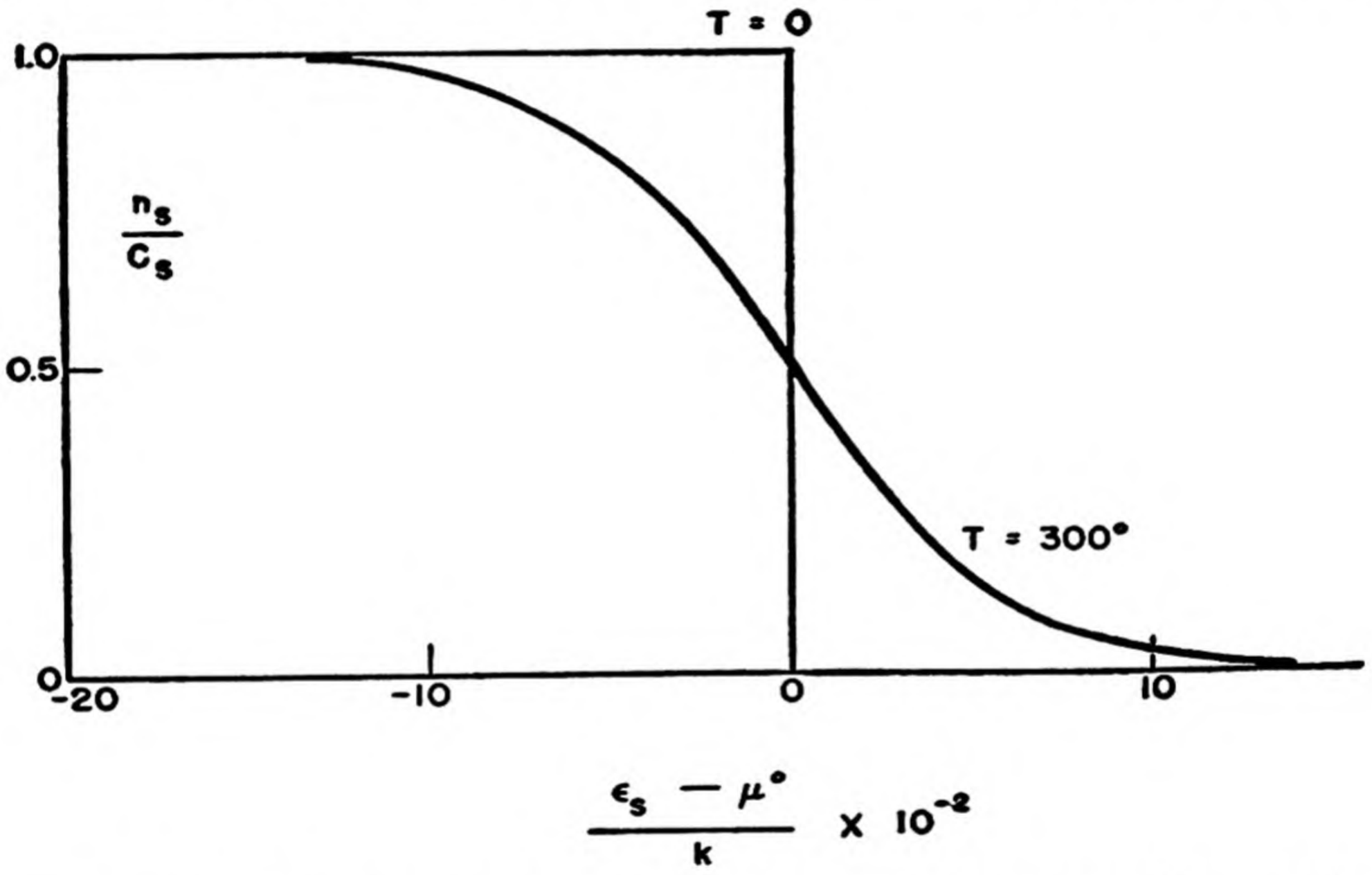



**Fig. 14.1.** Relative population of energy states according to the Fermi-Dirac distribution law. The curves extend much farther to the left than indicated.

only evaporate from the metal with the application of external radiant energy (photoelectric effect) or by raising the temperature to high values. This is because the attractive force of the positive metallic ions produces an electron work function of usually several electron volts.

Calculation of the pressure expected in $He^3$ at the absolute zero of temperature, using Eq. (14.3.7) and a molal volume of 38 cm.$^3$ (this is the molal volume at 1°K) yields a value of 4.18 atmospheres.

Actually at 1°K the vapor pressure[2] of $He^3$ is 8.7 mm. Hg, but a pressure of 29 atmospheres is required for production of solid $He^3$.

The low vapor pressure of $He^3$ at 1°K is due to the van der Waals attractive forces, which have been completely neglected in the derivation of Eq. (14.3.7) inasmuch as we have assumed in this chapter that all gas molecules behave ideally. We have also neglected zero point energies of vibration. The larger molal volume of liquid $He^3$, 38 ml. as compared with liquid $He^4$, 27.6 ml., is attributed to the higher zero point energy of $He^3$.

## PROBLEMS

**1.** Derive Eq. (14.3.4).

**2.** Find the average energy per mole of conduction electrons in potassium (density equal to 0.856) at the absolute zero of temperature. Express your answer in terms of $\mu^\circ$.

**3.** Show that for a Fermi gas at the absolute zero $P_0V_0 = \frac{2}{3}E_0$.

**4.** From the Bose-Einstein statistics, the thermodynamic probability $W_t$ is given by Eq. (14.2.3):

$$W_t = \prod_s \frac{(C_s + n_s - 1)!}{(C_s - 1)!n_s!}$$

Neglecting unity in comparison with $C_s$, demonstrate that

$$\ln W_t = \sum_s \bar{n}_s(1 - \ln \bar{n}_s)$$

where $\bar{n}_s$ equals $n_s/C_s$ and the summation is over all cells in all $s$ energy groups. *Hint:* $\ln (1 + \bar{n}_s) \cong \bar{n}_s$ inasmuch as the average occupation number of the cells $\bar{n}_s$ is very much smaller than unity under most circumstances.

# APPENDIX

*Table 1:*
VALUES OF USEFUL CONSTANTS

*Table 2:*
INTERNATIONAL ATOMIC WEIGHTS

*Table 3:*
SOME ISOTOPIC MASSES AND SPINS

*Table 4:*
CONVERSION FACTORS FOR UNITS OF MOLECULAR ENERGY

*Tables 5a, 5b, 5c:*
A SIX-PLACE TABLE OF THE EINSTEIN FUNCTIONS*

*Table 6:*
*G* FUNCTION OF BIGELEISEN AND MAYER

*Table 7:*
SOME USEFUL INTEGRALS

* Tables 5a, 5b, and 5c are reprinted by permission from the dissertation "A Six-Place Table of the Einstein Functions" by J. Sherman and R. B. Ewell, *J. Phys. Chem.*, Vol. 46, No. 6, June, 1942.

## Table 1. Values of Useful Constants[1]

| Name | Symbol | Value | Units |
|---|---|---|---|
| Velocity of light | $c$ | $2.99790 \times 10^{10}$ | cm/sec. |
| Planck constant | $h$ | $6.62377 \times 10^{-27}$ | erg sec./molecule |
| Avogadro constant | $N$ | $6.02380 \times 10^{23}$ | molecules/mole |
| Faraday constant | $\mathfrak{F}$ | 96,493.1 | coulombs/equiv. |
| | | 23,062.4 | cal./volt equiv. |
| Absolute temperature of the ice point | $T_{0°C}$ | 273.160 | °K |
| Electronic charge | $e = \mathfrak{F}/N$ | $1.60186 \times 10^{-19}$ | coulomb |
| | | $4.80223 \times 10^{-10}$ | e.s.u. |
| Gas constant | $R$ | 8.31439 | joules/deg. mole |
| | | 1.98719 | cal./deg. mole |
| | | 0.0820544 | liter atm./deg. mole |
| Boltzmann constant | $k = R/N$ | $1.38026 \times 10^{-16}$ | erg/deg. molecule |
| | $Nhc$ | 11.9617 | joule cm./mole |
| | | 2.85892 | cal. cm./mole |
| | $hc/k$ | 1.43868 | cm deg. |
| | $E/m = c^2$ | $8.98742 \times 10^{13}$ | joules/g. |
| Standard gravity | $g$ | 980.665 | cm./sec.$^2$ |
| Standard atmosphere | | 1,013,250 | dynes/cm.$^2$ |
| Thermochemical calories | | 4.1840 | joules (absolute) |
| | | 4.1833 | joules (international) |
| | | 0.0412917 | liter atm. |
| Dielectric constant of water at 25°C | $D_0$ | 78.54[a] | |

[a] B. E. Conway, *Electrochemical Data*, Elsevier Publishing Co., New York, 1952.

[1] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling, and G. W. Vinal, *J. Am. Chem. Soc.*, **74**, 2699 (1952).

## Table 2. International Atomic Weights (1953)[2]

| | Symbol | Atomic number | Atomic weight[a] |
|---|---|---|---|
| Actinium | Ac | 89 | 227 |
| Aluminum | Al | 13 | 26.98 |
| Americium | Am | 95 | [243] |
| Antimony | Sb | 51 | 121.76 |
| Argon | A | 18 | 39.944 |
| Arsenic | As | 33 | 74.91 |
| Astatine | At | 85 | [210] |
| Barium | Ba | 56 | 137.36 |
| Berkelium | Bk | 97 | [245] |
| Beryllium | Be | 4 | 9.013 |
| Bismuth | Bi | 83 | 209.00 |
| Boron | B | 5 | 10.82 |
| Bromine | Br | 35 | 79.916 |
| Cadmium | Cd | 48 | 112.41 |
| Calcium | Ca | 20 | 40.08 |
| Californium | Cf | 98 | [248] |
| Carbon | C | 6 | 12.011 |
| Cerium | Ce | 58 | 140.13 |
| Cesium | Cs | 55 | 132.91 |
| Chlorine | Cl | 17 | 35.457 |
| Chromium | Cr | 24 | 52.01 |
| Cobalt | Co | 27 | 58.94 |
| Copper | Cu | 29 | 63.54 |
| Curium | Cm | 96 | [245] |
| Dysprosium | Dy | 66 | 162.46 |
| Erbium | Er | 68 | 167.2 |
| Europium | Eu | 63 | 152.0 |
| Fluorine | F | 9 | 19.00 |
| Francium | Fr | 87 | [223] |
| Gadolinium | Gd | 64 | 156.9 |
| Gallium | Ga | 31 | 69.72 |
| Germanium | Ge | 32 | 72.60 |
| Gold | Au | 79 | 197.0 |
| Hafnium | Hf | 72 | 178.6 |
| Helium | He | 2 | 4.003 |
| Holmium | Ho | 67 | 164.94 |
| Hydrogen | H | 1 | 1.0080 |
| Indium | In | 49 | 114.76 |
| Iodine | I | 53 | 126.91 |
| Iridium | Ir | 77 | 192.2 |
| Iron | Fe | 26 | 55.85 |
| Krypton | Kr | 36 | 83.80 |
| Lanthanum | La | 57 | 138.92 |
| Lead | Pb | 82 | 207.21 |
| Lithium | Li | 3 | 6.940 |
| Lutetium | Lu | 71 | 174.99 |
| Magnesium | Mg | 12 | 24.32 |
| Manganese | Mn | 25 | 54.94 |
| Mercury | Hg | 80 | 200.61 |
| Molybdenum | Mo | 42 | 95.95 |
| Neodymium | Nd | 60 | 144.27 |
| Neptunium | Np | 93 | [237] |
| Neon | Ne | 10 | 20.183 |
| Nickel | Ni | 28 | 58.69 |
| Niobium (Columbium) | Nb | 41 | 92.91 |
| Nitrogen | N | 7 | 14.008 |
| Osmium | Os | 76 | 190.2 |
| Oxygen | O | 8 | 16 |
| Palladium | Pd | 46 | 106.7 |
| Phosphorus | P | 15 | 30.975 |
| Platinum | Pt | 78 | 195.23 |
| Plutonium | Pu | 94 | [242] |
| Polonium | Po | 84 | 210 |
| Potassium | K | 19 | 39.100 |
| Praseodymium | Pr | 59 | 140.92 |
| Promethium | Pm | 61 | [145] |
| Protactinium | Pa | 91 | 231 |
| Radium | Ra | 88 | 226.05 |
| Radon | Rn | 86 | 222 |
| Rhenium | Re | 75 | 186.31 |
| Rhodium | Rh | 45 | 102.91 |
| Rubidium | Rb | 37 | 85.48 |
| Ruthenium | Ru | 44 | 101.1 |
| Samarium | Sm | 62 | 150.43 |
| Scandium | Sc | 21 | 44.96 |
| Selenium | Se | 34 | 78.96 |
| Silicon | Si | 14 | 28.09 |
| Silver | Ag | 47 | 107.880 |
| Sodium | Na | 11 | 22.991 |
| Strontium | Sr | 38 | 87.63 |
| Sulfur | S | 16 | 32.066[b] |
| Tantalum | Ta | 73 | 180.88 |
| Technetium | Tc | 43 | [99] |
| Tellurium | Te | 52 | 127.61 |
| Terbium | Tb | 65 | 158.93 |
| Thallium | Tl | 81 | 204.39 |
| Thorium | Th | 90 | 232.05 |
| Thulium | Tm | 69 | 168.94 |
| Tin | Sn | 50 | 118.70 |
| Titanium | Ti | 22 | 47.90 |
| Tungsten | W | 74 | 183.92 |
| Uranium | U | 92 | 238.07 |
| Vanadium | V | 23 | 50.95 |
| Xenon | Xe | 54 | 131.3 |
| Ytterbium | Yb | 70 | 173.04 |
| Yttrium | Y | 39 | 88.92 |
| Zinc | Zn | 30 | 65.38 |
| Zirconium | Zr | 40 | 91.22 |

[a] A value given in brackets denotes the mass number of the isotope of longest known half-life.

[b] Because of natural variations in the relative abundances of the isotopes of sulfur the atomic weight of this element has a range of $\pm 0.003$.

[2] E. Wichers, *J. Am. Chem. Soc.*, in press.

## Table 3. Some Isotopic Masses and Spins[3]

| Isotope | Mass | Spin | Isotope | Mass | Spin |
|---|---|---|---|---|---|
| Electron | 0.0005486 | 1/2 | $F^{19}$ | 19.004456 | 1/2 |
| Neutron | 1.008982 | 1/2 | $Ne^{20}$ | 19.998774 | |
| $H^{1}$ | 1.008144 | 1/2 | $Ne^{21}$ | 21.000504 | 3/2 |
| $H^{2}$ | 2.014738 | 1 | $Ne^{22}$ | 21.998370 | |
| $H^{3}$ | 3.016997 | 1/2 | $Na^{23}$ | 22.997055 | 3/2 |
| $He^{3}$ | 3.016977 | 1/2 | $Mg^{24}$ | 23.992628 | 0 |
| $He^{4}$ | 4.003876 | 0 | $Mg^{25}$ | 24.993745 | |
| $Li^{6}$ | 6.017021 | 1 | $Mg^{26}$ | 25.990802 | |
| $Li^{7}$ | 7.018223 | 3/2 | $Al^{27}$ | 26.990090 | 5/2 |
| $Be^{9}$ | 9.015043 | 3/2 | $Si^{28}$ | 27.985796 | |
| $B^{10}$ | 10.016112 | 3 | $Si^{29}$ | 28.985677 | 1/2 |
| $B^{11}$ | 11.012800 | 3/2 | $Si^{30}$ | 29.983272 | |
| $C^{12}$ | 12.003824 | 0 | $P^{31}$ | 30.983584 | 1/2 |
| $C^{13}$ | 13.007489 | 1/2 | $S^{32}$ | 31.982228 | 0 |
| $N^{14}$ | 14.007532 | 1 | $S^{33}$ | 32.981911 | 3/2 |
| $N^{15}$ | 15.004882 | 1/2 | $S^{34}$ | 33.978709 | |
| $O^{16}$ | 16.000000 | 0 | $Cl^{35}$ | 34.98006 | 3/2 |
| $O^{17}$ | 17.004533 | 5/2 | $Cl^{37}$ | 36.97768 | 3/2 |
| $O^{18}$ | 18.004870 | 0 | | | |

[3] The isotopic masses were calculated from a table kindly submitted by T. L. Collins and A. O. Nier by averaging their values taken from nuclear-reaction mass tables and mass-spectrographic mass tables. The isotopic spins were taken from a table published by E. Segre, *Experimental Nuclear Physics*, John Wiley & Sons, New York, 1953, with the permission of the publisher.

## Table 4. Conversion Factors for Units of Molecular Energy[4]

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property expressed in one of the units in the top row of the table, multiply the former value by the factor in the block common to both units.

| Units ⟶ ↓ | | erg/molecule | abs joule/mole | int joule/mole | cal/mole | abs electron-volt/molecule | int electron-volt/molecule | wave no. ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 erg/molecule | = | 1 | $6.0235 \times 10^{16}$ | $6.0225 \times 10^{16}$ | $1.43965 \times 10^{16}$ | $6.2422 \times 10^{11}$ | $6.2402 \times 10^{11}$ | $5.0362 \times 10^{15}$ |
| 1 abs joule/mole | = | $1.66016 \times 10^{-17}$ | 1 | 0.999835 | 0.239006 | $1.03631 \times 10^{-5}$ | $1.03597 \times 10^{-5}$ | $8.3609 \times 10^{-2}$ |
| 1 int joule/mole | = | $1.66043 \times 10^{-17}$ | 1.000165 | 1 | 0.239046 | $1.03648 \times 10^{-5}$ | $1.03614 \times 10^{-5}$ | $8.3623 \times 10^{-2}$ |
| 1 cal/mole | = | $6.9461 \times 10^{-17}$ | 4.18400 | 4.1833 | 1 | $4.3359 \times 10^{-5}$ | $4.3345 \times 10^{-5}$ | 0.34982 |
| 1 abs electron-volt/molecule | = | $1.60199 \times 10^{-12}$ | 96,496 | 96,480 | 23,063.1 | 1 | 0.99967 | 8067.9 |
| 1 int electron-volt/molecule | = | $1.60252 \times 10^{-12}$ | 96,528 | 96,512 | 23,070.7 | 1.000330 | 1 | 8070.6 |
| 1 wave no. ($cm^{-1}$) | = | $1.98562 \times 10^{-16}$ | 11.9604 | 11.9584 | 2.85861 | $1.23947 \times 10^{-4}$ | $1.23906 \times 10^{-4}$ | 1 |

[4] F. D. Rossini, *Chemical Thermodynamics*, John Wiley & Sons, Inc., New York, 1950.

## Table 5a. A Six-Place Table of the Einstein Functions

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 0.000 | 1.000000 | 1.000000 | $\infty$ | 0.200 | 0.903331 | 0.996673 | 1.707772 |
| 0.005 | 0.997502 | 0.999998 | 5.300816 | 0.205 | 0.901000 | 0.996505 | 1.685495 |
| 0.010 | 0.995008 | 0.999992 | 4.610166 | 0.210 | 0.898672 | 0.996333 | 1.663811 |
| 0.015 | 0.992519 | 0.999981 | 4.207196 | 0.215 | 0.896349 | 0.996157 | 1.642692 |
| 0.020 | 0.990033 | 0.999967 | 3.922006 | 0.220 | 0.894030 | 0.995976 | 1.622112 |
| 0.025 | 0.987552 | 0.999948 | 3.701353 | 0.225 | 0.891715 | 0.995792 | 1.602046 |
| 0.030 | 0.985075 | 0.999925 | 3.521520 | 0.230 | 0.889404 | 0.995603 | 1.582473 |
| 0.035 | 0.982602 | 0.999898 | 3.369856 | 0.235 | 0.887098 | 0.995411 | 1.563370 |
| 0.040 | 0.980133 | 0.999867 | 3.238809 | 0.240 | 0.884795 | 0.995214 | 1.544717 |
| 0.045 | 0.977669 | 0.999831 | 3.123508 | 0.245 | 0.882497 | 0.995013 | 1.526497 |
| 0.050 | 0.975208 | 0.999792 | 3.020628 | 0.250 | 0.880203 | 0.994808 | 1.508691 |
| 0.055 | 0.972752 | 0.999748 | 2.927796 | 0.255 | 0.877913 | 0.994599 | 1.491284 |
| 0.060 | 0.970300 | 0.999700 | 2.843261 | 0.260 | 0.875627 | 0.994386 | 1.474259 |
| 0.065 | 0.967852 | 0.999648 | 2.765692 | 0.265 | 0.873345 | 0.994168 | 1.457601 |
| 0.070 | 0.965408 | 0.999592 | 2.694056 | 0.270 | 0.871068 | 0.993947 | 1.441298 |
| 0.075 | 0.962969 | 0.999531 | 2.627533 | 0.275 | 0.868794 | 0.993722 | 1.425335 |
| 0.080 | 0.960533 | 0.999467 | 2.565462 | 0.280 | 0.866525 | 0.993492 | 1.409701 |
| 0.085 | 0.958102 | 0.999398 | 2.507303 | 0.285 | 0.864260 | 0.993259 | 1.394384 |
| 0.090 | 0.955675 | 0.999325 | 2.452608 | 0.290 | 0.861999 | 0.993021 | 1.379373 |
| 0.095 | 0.953252 | 0.999248 | 2.401002 | 0.295 | 0.859742 | 0.992779 | 1.364656 |
| 0.100 | 0.950833 | 0.999167 | 2.352168 | 0.300 | 0.857489 | 0.992534 | 1.350226 |
| 0.105 | 0.948419 | 0.999082 | 2.305836 | 0.305 | 0.855240 | 0.992284 | 1.336070 |
| 0.110 | 0.946008 | 0.998992 | 2.261771 | 0.310 | 0.852996 | 0.992030 | 1.322182 |
| 0.115 | 0.943602 | 0.998899 | 2.219772 | 0.315 | 0.850755 | 0.991772 | 1.308552 |
| 0.120 | 0.941200 | 0.998801 | 2.179664 | 0.320 | 0.848519 | 0 991510 | 1.295171 |
| 0.125 | 0.938802 | 0.998699 | 2.141291 | 0.325 | 0.846287 | 0.991244 | 1.282033 |
| 0.130 | 0.936408 | 0.998593 | 2.104517 | 0.330 | 0.844059 | 0.990974 | 1.269129 |
| 0.135 | 0.934018 | 0.998483 | 2.069221 | 0.335 | 0.841835 | 0.990700 | 1.256453 |
| 0.140 | 0.931633 | 0.998368 | 2.035296 | 0.340 | 0.839615 | 0.990422 | 1.243998 |
| 0.145 | 0.929251 | 0.998250 | 2.002646 | 0.345 | 0.837399 | 0.990140 | 1.231756 |
| 0.150 | 0.926874 | 0.998127 | 1.971183 | 0.350 | 0.835188 | 0.989854 | 1.219723 |
| 0.155 | 0 924501 | 0.998000 | 1.940829 | 0.355 | 0 832980 | 0.989564 | 1 207892 |
| 0.160 | 0.922132 | 0.997869 | 1.911515 | 0.360 | 0.830777 | 0.989270 | 1.196257 |
| 0.165 | 0.919768 | 0.997734 | 1.883176 | 0.365 | 0.828578 | 0.988971 | 1.184813 |
| 0.170 | 0.917407 | 0.997595 | 1.855753 | 0.370 | 0.826382 | 0.988669 | 1.173555 |
| 0.175 | 0.915051 | 0.997452 | 1 829194 | 0.375 | 0.824191 | 0.988363 | 1.162477 |
| 0.180 | 0.912699 | 0.997304 | 1.803449 | 0.380 | 0.822004 | 0.988053 | 1.151575 |
| 0.185 | 0.910350 | 0.997153 | 1.778474 | 0.385 | 0.319822 | 0.987739 | 1.140844 |
| 0.190 | 0.908007 | 0.996997 | 1.754227 | 0.390 | 0.817643 | 0.987421 | 1.130279 |
| 0.195 | 0.905667 | 0.996837 | 1.730672 | 0.395 | 0.815468 | 0.987099 | 1.119877 |

## Table 5a (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 0.400 | 0.813298 | 0.986773 | 1.109633 | 0.600 | 0.729822 | 0.970532 | 0.795870 |
| 0.405 | 0.811132 | 0.986443 | 1.099543 | 0.605 | 0.727818 | 0.970048 | 0.789822 |
| 0.410 | 0.808969 | 0.986109 | 1.089604 | 0.610 | 0.725818 | 0.969560 | 0.783840 |
| 0.415 | 0.806811 | 0.985771 | 1.079811 | 0.615 | 0.723822 | 0.969068 | 0.777923 |
| 0.420 | 0.804657 | 0.985429 | 1.070161 | 0.620 | 0.721830 | 0.968573 | 0.772070 |
| 0.425 | 0.802507 | 0.985083 | 1.060651 | 0.625 | 0.719842 | 0.968074 | 0.766280 |
| 0.430 | 0.800361 | 0.984733 | 1.051278 | 0.630 | 0.717858 | 0.967571 | 0.760552 |
| 0.435 | 0.798219 | 0.984379 | 1.042037 | 0.635 | 0.715878 | 0.967065 | 0.754885 |
| 0.440 | 0.796082 | 0.984022 | 1.032927 | 0.640 | 0.713903 | 0.966555 | 0.749278 |
| 0.445 | 0.793948 | 0.983660 | 1.023944 | 0.645 | 0.711931 | 0.966041 | 0.743730 |
| 0.450 | 0.791818 | 0.983294 | 1.015085 | 0.650 | 0.709963 | 0.965523 | 0.738240 |
| 0.455 | 0.789693 | 0.982925 | 1.006347 | 0.655 | 0.707999 | 0.965002 | 0.732807 |
| 0.460 | 0.787571 | 0.982552 | 0.997728 | 0.660 | 0.706039 | 0.964477 | 0.727431 |
| 0.465 | 0.785454 | 0.982174 | 0.989225 | 0.665 | 0.704083 | 0.963949 | 0.722110 |
| 0.470 | 0.783341 | 0.981793 | 0.980835 | 0.670 | 0.702131 | 0.963417 | 0.716843 |
| 0.475 | 0.781232 | 0.981408 | 0.972557 | 0.675 | 0.700184 | 0.962881 | 0.711630 |
| 0.480 | 0.779127 | 0.981019 | 0.964388 | 0.680 | 0.698240 | 0.962341 | 0.706469 |
| 0.485 | 0.777026 | 0.980626 | 0.956324 | 0.685 | 0.696300 | 0.961798 | 0.701361 |
| 0.490 | 0.774929 | 0.980230 | 0.948366 | 0.690 | 0.694364 | 0.961252 | 0.696304 |
| 0.495 | 0.772836 | 0.979829 | 0.940509 | 0.695 | 0.692432 | 0.960702 | 0.691298 |
| 0.500 | 0.770747 | 0.979425 | 0.932752 | 0.700 | 0.690504 | 0.960148 | 0.686341 |
| 0.505 | 0.768662 | 0.979016 | 0.925093 | 0.705 | 0.688580 | 0.959591 | 0.681433 |
| 0.510 | 0.766582 | 0.978604 | 0.917530 | 0.710 | 0.686660 | 0.959030 | 0.676574 |
| 0.515 | 0.764505 | 0.978188 | 0.910062 | 0.715 | 0.684743 | 0.958465 | 0.671762 |
| 0.520 | 0.762432 | 0.977768 | 0.902685 | 0.720 | 0.682831 | 0.957897 | 0.666997 |
| 0.525 | 0.760364 | 0.977344 | 0.895399 | 0.725 | 0.680923 | 0.957326 | 0.662278 |
| 0.530 | 0.758299 | 0.976917 | 0.888201 | 0.730 | 0.679019 | 0.956750 | 0.657604 |
| 0.535 | 0.756239 | 0.976485 | 0.881091 | 0.735 | 0.677119 | 0.956172 | 0.652976 |
| 0.540 | 0.754183 | 0.976050 | 0.874965 | 0.740 | 0.675222 | 0.955589 | 0.648392 |
| 0.545 | 0.752130 | 0.975611 | 0.867124 | 0.745 | 0.673330 | 0.955004 | 0.643851 |
| 0.550 | 0.750082 | 0.975168 | 0.860264 | 0.750 | 0.671441 | 0.954415 | 0.639354 |
| 0.555 | 0.748038 | 0.974722 | 0.853486 | 0.755 | 0.669557 | 0.953822 | 0.634898 |
| 0.560 | 0.745998 | 0.974271 | 0.846786 | 0.760 | 0.667676 | 0.953226 | 0.630485 |
| 0.565 | 0.743962 | 0.973817 | 0.840164 | 0.765 | 0.665800 | 0.952626 | 0.626113 |
| 0.570 | 0.741930 | 0.973359 | 0.833618 | 0.770 | 0.663927 | 0.952023 | 0.621781 |
| 0.575 | 0.739901 | 0.972897 | 0.827147 | 0.775 | 0.662058 | 0.951416 | 0.617490 |
| 0.580 | 0.737877 | 0.972432 | 0.820750 | 0.780 | 0.660193 | 0.950806 | 0.613239 |
| 0.585 | 0.735857 | 0.971963 | 0.814424 | 0.785 | 0.658332 | 0.950192 | 0.609026 |
| 0.590 | 0.733841 | 0.971490 | 0.808170 | 0.790 | 0.656475 | 0.949575 | 0.604852 |
| 0.595 | 0.731829 | 0.971013 | 0.801986 | 0.795 | 0.654622 | 0.948955 | 0.600716 |

## Table 5a (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2e^x}{(e^x - 1)^2}$ | $-\ln(1 - e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 0.800 | 0.652773 | 0.948331 | 0.596618 | 1.000 | 0.581977 | 0.920674 | 0.458675 |
| 0.805 | 0.650928 | 0.947704 | 0.592556 | 1.005 | 0.580285 | 0.919917 | 0.455777 |
| 0.810 | 0.649086 | 0.947073 | 0.588531 | 1.010 | 0.578597 | 0.919158 | 0.452901 |
| 0.815 | 0.647249 | 0.946439 | 0.584543 | 1.015 | 0.576913 | 0.918396 | 0.450048 |
| 0.820 | 0.645415 | 0.945801 | 0.580590 | 1.020 | 0.575233 | 0.917630 | 0.447217 |
| 0.825 | 0.643586 | 0.945161 | 0.576672 | 1.025 | 0.573556 | 0.916862 | 0.444408 |
| 0.830 | 0.641760 | 0.944516 | 0.572788 | 1.030 | 0.571884 | 0.916091 | 0.441621 |
| 0.835 | 0.639938 | 0.943869 | 0.568939 | 1.035 | 0.570215 | 0.915317 | 0.438856 |
| 0.840 | 0.638120 | 0.943218 | 0.565124 | 1.040 | 0.568549 | 0.914540 | 0.436112 |
| 0.845 | 0.636306 | 0.942564 | 0.561343 | 1.045 | 0.566888 | 0.913759 | 0.433389 |
| 0.850 | 0.634496 | 0.941906 | 0.557594 | 1.050 | 0.565230 | 0.912976 | 0.430687 |
| 0.855 | 0.632689 | 0.941245 | 0.553878 | 1.055 | 0.563576 | 0.912190 | 0.428006 |
| 0.860 | 0.630887 | 0.940581 | 0.550194 | 1.060 | 0.561926 | 0.911401 | 0.425345 |
| 0.865 | 0.629088 | 0.939913 | 0.546542 | 1.065 | 0.560279 | 0.910610 | 0.422705 |
| 0.870 | 0.627293 | 0.939242 | 0.542921 | 1.070 | 0.558636 | 0.909815 | 0.420084 |
| 0.875 | 0.625503 | 0.938568 | 0.539331 | 1.075 | 0.556997 | 0.909017 | 0.417484 |
| 0.880 | 0.623715 | 0.937891 | 0.535772 | 1.080 | 0.555361 | 0.908217 | 0.414903 |
| 0.885 | 0.621932 | 0.937210 | 0.532244 | 1.085 | 0.553730 | 0.907413 | 0.412341 |
| 0.890 | 0.620153 | 0.936526 | 0.528745 | 1.090 | 0.552102 | 0.906607 | 0.409799 |
| 0.895 | 0.618378 | 0.935839 | 0.525276 | 1.095 | 0.550477 | 0.905798 | 0.407276 |
| 0.900 | 0.616606 | 0.935148 | 0.521835 | 1.100 | 0.548857 | 0.904986 | 0.404772 |
| 0.905 | 0.614838 | 0.934455 | 0.518424 | 1.105 | 0.547240 | 0.904171 | 0.402286 |
| 0.910 | 0.613074 | 0.933758 | 0.515041 | 1.110 | 0.545627 | 0.903354 | 0.399819 |
| 0.915 | 0.611314 | 0.933058 | 0.511687 | 1.115 | 0.544017 | 0.902534 | 0.397371 |
| 0.920 | 0.609558 | 0.932354 | 0.508360 | 1.120 | 0.542411 | 0.901710 | 0.394940 |
| 0.925 | 0.607806 | 0.931648 | 0.505061 | 1.125 | 0.540809 | 0.900884 | 0.392528 |
| 0.930 | 0.606057 | 0.930938 | 0.501789 | 1.130 | 0.539211 | 0.900056 | 0.390133 |
| 0.935 | 0.604312 | 0.930228 | 0.498544 | 1.135 | 0.537616 | 0.899224 | 0.387756 |
| 0.940 | 0.602571 | 0.929509 | 0.495326 | 1.140 | 0.536025 | 0.898390 | 0.385396 |
| 0.945 | 0.600834 | 0.928790 | 0.492134 | 1.145 | 0.534437 | 0.897553 | 0.383054 |
| 0.950 | 0.599101 | 0.928068 | 0.488968 | 1.150 | 0.532853 | 0.896714 | 0.380729 |
| 0.955 | 0.597371 | 0.927342 | 0.485828 | 1.155 | 0.531273 | 0.895871 | 0.378420 |
| 0.960 | 0.595646 | 0.926614 | 0.482713 | 1.160 | 0.529696 | 0.895026 | 0.376129 |
| 0.965 | 0.593924 | 0.925882 | 0.479623 | 1.165 | 0.528124 | 0.894179 | 0.373854 |
| 0.970 | 0.592206 | 0.925147 | 0.476558 | 1.170 | 0.526554 | 0.893328 | 0.371596 |
| 0.975 | 0.590491 | 0.924409 | 0.473518 | 1.175 | 0.524989 | 0.892475 | 0.369353 |
| 0.980 | 0.588781 | 0.923668 | 0.470502 | 1.180 | 0.523427 | 0.891619 | 0.367128 |
| 0.985 | 0.587074 | 0.922924 | 0.467510 | 1.185 | 0.521869 | 0.890761 | 0.364918 |
| 0.990 | 0.585363 | 0.922159 | 0.464541 | 1.190 | 0.520314 | 0.889900 | 0.362724 |
| 0.995 | 0.583672 | 0.921427 | 0.461597 | 1.195 | 0.518763 | 0.889036 | 0.360545 |

## Table 5a (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{\bar{x}}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 1.200 | 0.517215 | 0.888170 | 0.358382 | 1.400 | 0.458235 | 0.851509 | 0.283155 |
| 1.205 | 0.515671 | 0.887301 | 0.356235 | 1.405 | 0.456832 | 0.850545 | 0.281524 |
| 1.210 | 0.514131 | 0.886430 | 0.354103 | 1.410 | 0.455433 | 0.849580 | 0.279903 |
| 1.215 | 0.512595 | 0.885556 | 0.351986 | 1.415 | 0.454037 | 0.848612 | 0.278294 |
| 1.220 | 0.511062 | 0.884679 | 0.349884 | 1.420 | 0.452644 | 0.847642 | 0.276695 |
| 1.225 | 0.509532 | 0.883800 | 0.347797 | 1.425 | 0.451255 | 0.846670 | 0.275106 |
| 1.230 | 0.508006 | 0.882918 | 0.345724 | 1.430 | 0.449870 | 0.845696 | 0.273528 |
| 1.235 | 0.506484 | 0.882034 | 0.343667 | 1.435 | 0.448487 | 0.844720 | 0.271960 |
| 1.240 | 0.504965 | 0.881147 | 0.341623 | 1.440 | 0.447108 | 0.843742 | 0.270403 |
| 1.245 | 0.503450 | 0.880258 | 0.339594 | 1.445 | 0.445733 | 0.842762 | 0.268855 |
| 1.250 | 0.501939 | 0.879366 | 0.337580 | 1.450 | 0.444361 | 0.841780 | 0.267318 |
| 1.255 | 0.500431 | 0.878472 | 0.335579 | 1.455 | 0.442992 | 0.840795 | 0.265791 |
| 1.260 | 0.498927 | 0.877575 | 0.333592 | 1.460 | 0.441627 | 0.839809 | 0.264273 |
| 1.265 | 0.497426 | 0.876676 | 0.331619 | 1.465 | 0.440265 | 0.838821 | 0.262766 |
| 1.270 | 0.495929 | 0.875774 | 0.329660 | 1.470 | 0.438906 | 0.837831 | 0.261268 |
| 1.275 | 0.494435 | 0.874870 | 0.327714 | 1.475 | 0.437551 | 0.836839 | 0.259780 |
| 1.280 | 0.492945 | 0.873964 | 0.325782 | 1.480 | 0.436199 | 0.835844 | 0.258301 |
| 1.285 | 0.491458 | 0.873055 | 0.323863 | 1.485 | 0.434851 | 0.834848 | 0.256833 |
| 1.290 | 0.489975 | 0.872144 | 0.321957 | 1.490 | 0.433506 | 0.833850 | 0.255373 |
| 1.295 | 0.488496 | 0.871230 | 0.320065 | 1.495 | 0.432164 | 0.832850 | 0.253923 |
| 1.300 | 0.487020 | 0.870314 | 0.318185 | 1.500 | 0.430825 | 0.831849 | 0.252482 |
| 1.305 | 0.485547 | 0.869395 | 0.316318 | 1.505 | 0.429490 | 0.830845 | 0.251051 |
| 1.310 | 0.484078 | 0.868474 | 0.314464 | 1.510 | 0.428159 | 0.829839 | 0.249629 |
| 1.315 | 0.482613 | 0.867551 | 0.312623 | 1.515 | 0.426830 | 0.828832 | 0.248215 |
| 1.320 | 0.481151 | 0.866626 | 0.310794 | 1.520 | 0.425505 | 0.827822 | 0.246811 |
| 1.325 | 0.479693 | 0.865698 | 0.308978 | 1.525 | 0.424183 | 0.826811 | 0.245416 |
| 1.330 | 0.478238 | 0.864768 | 0.307174 | 1.530 | 0.422865 | 0.825798 | 0.244030 |
| 1.335 | 0.476786 | 0.863835 | 0.305382 | 1.535 | 0.421550 | 0.824783 | 0.242652 |
| 1.340 | 0.475339 | 0.862900 | 0.303602 | 1.540 | 0.420238 | 0.823766 | 0.241283 |
| 1.345 | 0.473894 | 0.861963 | 0.301835 | 1.545 | 0.418929 | 0.822748 | 0.239923 |
| 1.350 | 0.472453 | 0.861024 | 0.300079 | 1.550 | 0.417624 | 0.821728 | 0.238572 |
| 1.355 | 0.471016 | 0.860082 | 0.298335 | 1.555 | 0.416322 | 0.820706 | 0.237229 |
| 1.360 | 0.469582 | 0.859139 | 0.296603 | 1.560 | 0.415024 | 0.819682 | 0.235895 |
| 1.365 | 0.468151 | 0.858193 | 0.294882 | 1.565 | 0.413728 | 0.818656 | 0.234569 |
| 1.370 | 0.466724 | 0.857244 | 0.293173 | 1.570 | 0.412436 | 0.817629 | 0.233251 |
| 1.375 | 0.465301 | 0.856294 | 0.291475 | 1.575 | 0.411148 | 0.816600 | 0.231942 |
| 1.380 | 0.463881 | 0.855341 | 0.289789 | 1.580 | 0.409862 | 0.815569 | 0.230640 |
| 1.385 | 0.462464 | 0.854386 | 0.288114 | 1.585 | 0.408580 | 0.814536 | 0.229348 |
| 1.390 | 0.461051 | 0.853429 | 0.286450 | 1.590 | 0.407301 | 0.813502 | 0.228063 |
| 1.395 | 0.459641 | 0.852470 | 0.284797 | 1.595 | 0.406025 | 0.812466 | 0.226786 |

Table 5a (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 1.600 | 0.404753 | 0.811429 | 0.225517 | 1.800 | 0.356461 | 0.768693 | 0.180682 |
| 1.605 | 0.403483 | 0.810390 | 0 224256 | 1.805 | 0.355317 | 0 767597 | 0.179694 |
| 1.610 | 0 402217 | 0 809349 | 0.223003 | 1.810 | 0.354176 | 0.766500 | 0.178713 |
| 1 615 | 0.400955 | 0 808306 | 0 221758 | 1.815 | 0.353039 | 0.765402 | 0 177738 |
| 1 620 | 0 399695 | 0 807262 | 0 220520 | 1.820 | 0.351904 | 0.764303 | 0 176770 |
| 1.625 | 0 398439 | 0 806216 | 0 219291 | 1.825 | 0.350773 | 0.763202 | 0.175804 |
| 1 630 | 0 397186 | 0 805169 | 0 218068 | 1.830 | 0.349645 | 0.762101 | 0.174846 |
| 1.635 | 0 395936 | 0 804120 | 0.216854 | 1.835 | 0.348519 | 0.760998 | 0.173893 |
| 1 640 | 0 394689 | 0 803070 | 0.215647 | 1.840 | 0.347397 | 0.759894 | 0.172947 |
| 1 645 | 0 393446 | 0 802017 | 0 214447 | 1.845 | 0.346277 | 0.758790 | 0.172005 |
| 1 650 | 0 392205 | 0 800964 | 0.213255 | 1.850 | 0.345161 | 0.757684 | 0.171070 |
| 1 655 | 0 390968 | 0 799909 | 0.212070 | 1.855 | 0.344047 | 0.756577 | 0.170140 |
| 1 660 | 0 389734 | 0 798852 | 0.210893 | 1.860 | 0.342937 | 0.755469 | 0.169215 |
| 1.665 | 0 388504 | 0 797794 | 0 209722 | 1.865 | 0.341830 | 0.754360 | 0.168296 |
| 1 670 | 0 387276 | 0 796734 | 0.208559 | 1.870 | 0.340725 | 0.753249 | 0.167382 |
| 1 675 | 0 386052 | 0 795673 | 0 207403 | 1.875 | 0.339624 | 0.752138 | 0.166474 |
| 1 680 | 0 384831 | 0 794610 | 0 206254 | 1.880 | 0.338525 | 0.751026 | 0.165571 |
| 1 685 | 0 383613 | 0 793546 | 0 205113 | 1.885 | 0.337429 | 0.749913 | 0.164673 |
| 1 690 | 0 382398 | 0 792481 | 0 203978 | 1.890 | 0.336337 | 0.748799 | 0.163781 |
| 1 695 | 0 381186 | 0 791413 | 0 202850 | 1.895 | 0.335247 | 0 747684 | 0.162894 |
| 1 700 | 0 379978 | 0 790345 | 0.201729 | 1.900 | 0.334160 | 0.746568 | 0.162012 |
| 1.705 | 0 378772 | 0 789275 | 0.200615 | 1.905 | 0.333076 | 0.745451 | 0.161135 |
| 1 710 | 0 377570 | 0 788204 | 0.199507 | 1.910 | 0.331996 | 0.744333 | 0.160263 |
| 1 715 | 0 376371 | 0 787131 | 0.198407 | 1.915 | 0.330918 | 0.743214 | 0.159397 |
| 1 720 | 0 375175 | 0 786057 | 0 197313 | 1.920 | 0.329843 | 0.742094 | 0.158535 |
| 1.725 | 0.373982 | 0 784982 | 0.196225 | 1.925 | 0.328770 | 0.740973 | 0.157679 |
| 1 730 | 0 372792 | 0 783905 | 0 195145 | 1.930 | 0.327701 | 0.739852 | 0.156827 |
| 1 735 | 0 371606 | 0 782827 | 0.194071 | 1.935 | 0.326635 | 0.738729 | 0.155981 |
| 1 740 | 0 370422 | 0 781747 | 0.193003 | 1.940 | 0.325572 | 0.737606 | 0.155139 |
| 1 745 | 0 369242 | 0 780666 | 0.191942 | 1.945 | 0.324511 | 0.736482 | 0.154302 |
| 1 750 | 0 368064 | 0.779584 | 0.190887 | 1.950 | 0.323453 | 0.735356 | 0.153471 |
| 1 755 | 0 366890 | 0 778501 | 0 189838 | 1.955 | 0.322399 | 0.734231 | 0.152644 |
| 1.760 | 0 365719 | 0.777416 | 0.188796 | 1.960 | 0.321347 | 0.733104 | 0.151821 |
| 1.765 | 0 364551 | 0.776330 | 0.187761 | 1.965 | 0.320298 | 0.731976 | 0.151004 |
| 1.770 | 0 363386 | 0.775243 | 0.186731 | 1.970 | 0.319252 | 0.730848 | 0.150191 |
| 1 775 | 0.362224 | 0.774154 | 0.185707 | 1.975 | 0.318209 | 0.729719 | 0.149384 |
| 1.780 | 0 361065 | 0 773064 | 0.184690 | 1.980 | 0.317168 | 0.728589 | 0.148580 |
| 1.785 | 0 359910 | 0 771973 | 0.183679 | 1.985 | 0.316131 | 0.727458 | 0.147782 |
| 1.790 | 0.358757 | 0.770881 | 0.182674 | 1.990 | 0.315096 | 0.726327 | 0.146988 |
| 1.795 | 0 357607 | 0.769788 | 0.181675 | 1.995 | 0.314064 | 0.725195 | 0.146198 |

## Table 5a (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 2.000 | 0.313035 | 0.724062 | 0.145413 | 2.200 | 0.274143 | 0.678269 | 0.117436 |
| 2.005 | 0.312009 | 0.722928 | 0.144633 | 2.205 | 0.273226 | 0.677115 | 0.116815 |
| 2.010 | 0.310986 | 0.721794 | 0.143857 | 2.210 | 0.272311 | 0.675961 | 0.116197 |
| 2.015 | 0.309965 | 0.720659 | 0.143086 | 2.215 | 0.271399 | 0.674807 | 0.115583 |
| 2.020 | 0.308948 | 0.719523 | 0.142319 | 2.220 | 0.270490 | 0.673652 | 0.114972 |
| 2.025 | 0.307933 | 0.718386 | 0.141556 | 2.225 | 0.269583 | 0.672498 | 0.114365 |
| 2.030 | 0.306921 | 0.717249 | 0.140798 | 2.230 | 0.268679 | 0.671343 | 0.113761 |
| 2.035 | 0.305911 | 0.716112 | 0.140044 | 2.235 | 0.267777 | 0.670187 | 0.113160 |
| 2.040 | 0.304905 | 0.714973 | 0.139295 | 2.240 | 0.266879 | 0.669032 | 0.112562 |
| 2.045 | 0.303901 | 0.713834 | 0.138550 | 2.245 | 0.265982 | 0.667876 | 0.111968 |
| 2.050 | 0.302900 | 0.712695 | 0.137809 | 2.250 | 0.265088 | 0.666721 | 0.111378 |
| 2.055 | 0.301902 | 0.711554 | 0.137072 | 2.255 | 0.264197 | 0.665565 | 0.110790 |
| 2.060 | 0.300907 | 0.710413 | 0.136340 | 2.260 | 0.263308 | 0.664408 | 0.110206 |
| 2.065 | 0.299914 | 0.709272 | 0.135611 | 2.265 | 0.262422 | 0.663252 | 0.109625 |
| 2.070 | 0.298925 | 0.708130 | 0.134887 | 2.270 | 0.261539 | 0.662096 | 0.109047 |
| 2.075 | 0.297938 | 0.706987 | 0.134168 | 2.275 | 0.260658 | 0.660939 | 0.108473 |
| 2.080 | 0.296953 | 0.705844 | 0.133452 | 2.280 | 0.259779 | 0.659782 | 0.107902 |
| 2.085 | 0.295972 | 0.704700 | 0.132740 | 2.285 | 0.258903 | 0.658625 | 0.107334 |
| 2.090 | 0.294993 | 0.703556 | 0.132032 | 2.290 | 0.258030 | 0.657468 | 0.106769 |
| 2.095 | 0.294017 | 0.702411 | 0.131328 | 2.295 | 0.257159 | 0.656311 | 0.106207 |
| 2.100 | 0.293044 | 0.701266 | 0.130629 | 2.300 | 0.256291 | 0.655154 | 0.105648 |
| 2.105 | 0.292073 | 0.700120 | 0.129932 | 2.305 | 0.255425 | 0.653996 | 0.105092 |
| 2.110 | 0.291105 | 0.698974 | 0.129240 | 2.310 | 0.254562 | 0.652839 | 0.104539 |
| 2.115 | 0.290140 | 0.697827 | 0.128553 | 2.315 | 0.253701 | 0.651681 | 0.103990 |
| 2.120 | 0.289177 | 0.696680 | 0.127869 | 2.320 | 0.252842 | 0.650524 | 0.103444 |
| 2.125 | 0.288218 | 0.695532 | 0.127189 | 2.325 | 0.251987 | 0.649366 | 0.102901 |
| 2.130 | 0.287261 | 0.694384 | 0.126512 | 2.330 | 0.251133 | 0.648209 | 0.102361 |
| 2.135 | 0.286306 | 0.693235 | 0.125840 | 2.335 | 0.250282 | 0.647051 | 0.101824 |
| 2.140 | 0.285355 | 0.692086 | 0.125172 | 2.340 | 0.249434 | 0.645893 | 0.101290 |
| 2.145 | 0.284406 | 0.690937 | 0.124507 | 2.345 | 0.248588 | 0.644735 | 0.100758 |
| 2.150 | 0.283459 | 0.689787 | 0.123846 | 2.350 | 0.247745 | 0.643578 | 0.100229 |
| 2.155 | 0.282516 | 0.688637 | 0.123189 | 2.355 | 0.246904 | 0.642420 | 0.099703 |
| 2.160 | 0.281575 | 0.687486 | 0.122535 | 2.360 | 0.246065 | 0.641262 | 0.099180 |
| 2.165 | 0.280637 | 0.686335 | 0.121885 | 2.365 | 0.245229 | 0.640104 | 0.098660 |
| 2.170 | 0.279701 | 0.685184 | 0.121239 | 2.370 | 0.244396 | 0.638947 | 0.098143 |
| 2.175 | 0.278768 | 0.684032 | 0.120596 | 2.375 | 0.243564 | 0.637789 | 0.097629 |
| 2.180 | 0.277838 | 0.682880 | 0.119957 | 2.380 | 0.242736 | 0.636632 | 0.097118 |
| 2.185 | 0.276910 | 0.681728 | 0.119321 | 2.385 | 0.241909 | 0.635474 | 0.096609 |
| 2.190 | 0.275985 | 0.680575 | 0.118690 | 2.390 | 0.241086 | 0.634317 | 0.096103 |
| 2.195 | 0.275063 | 0.679422 | 0.118061 | 2.395 | 0.240264 | 0.633159 | 0.095600 |

## Table 5a (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 2.400 | 0.239445 | 0.632002 | 0.095100 | 2.600 | 0.208605 | 0.585890 | 0.077177 |
| 2.405 | 0.238628 | 0.630845 | 0.094602 | 2.605 | 0.207881 | 0.584744 | 0.076776 |
| 2.410 | 0.237814 | 0.629688 | 0.094108 | 2.610 | 0.207158 | 0.583598 | 0.076379 |
| 2.415 | 0.237002 | 0.628531 | 0.093616 | 2.615 | 0.206438 | 0.582453 | 0.075983 |
| 2.420 | 0.236193 | 0.627374 | 0.093126 | 2.620 | 0.205721 | 0.581309 | 0.075589 |
| 2.425 | 0.235386 | 0.626217 | 0.092640 | 2.625 | 0.205005 | 0.580165 | 0.075198 |
| 2.430 | 0.234581 | 0.625061 | 0.092156 | 2.630 | 0.204291 | 0.579021 | 0.074808 |
| 2.435 | 0.233779 | 0.623905 | 0.091674 | 2.635 | 0.203580 | 0.577878 | 0.074421 |
| 2.440 | 0.232979 | 0.622748 | 0.091195 | 2.640 | 0.202871 | 0.576736 | 0.074035 |
| 2.445 | 0.232182 | 0.621592 | 0.090719 | 2.645 | 0.202164 | 0.575594 | 0.073652 |
| 2.450 | 0.231386 | 0.620436 | 0.090246 | 2.650 | 0.201459 | 0.574452 | 0.073271 |
| 2.455 | 0.230594 | 0.619281 | 0.089775 | 2.655 | 0.200756 | 0.573311 | 0.072892 |
| 2.460 | 0.229803 | 0.518125 | 0.089307 | 2.660 | 0.200056 | 0.572171 | 0.072515 |
| 2.465 | 0.229015 | 0.616970 | 0.088841 | 2.665 | 0.199357 | 0.571031 | 0.072140 |
| 2.470 | 0.228229 | 0.615815 | 0.088378 | 2.670 | 0.198661 | 0.569892 | 0.071767 |
| 2.475 | 0.227446 | 0.614660 | 0.087917 | 2.675 | 0.197967 | 0.568753 | 0.071396 |
| 2.480 | 0.226665 | 0.613506 | 0.087459 | 2.680 | 0.197275 | 0.567615 | 0.071027 |
| 2.485 | 0.225886 | 0.612351 | 0.087003 | 2.685 | 0.196585 | 0.566477 | 0.070660 |
| 2.490 | 0.225110 | 0.611197 | 0.086550 | 2.690 | 0.195897 | 0.565340 | 0.070295 |
| 2.495 | 0.224336 | 0.610044 | 0.086099 | 2.695 | 0.195212 | 0.564203 | 0.069932 |
| 2.500 | 0.223564 | 0.608890 | 0.085650 | 2.700 | 0.194528 | 0.563068 | 0.069570 |
| 2.505 | 0.222794 | 0.607737 | 0.085204 | 2.705 | 0.193847 | 0.561932 | 0.069211 |
| 2.510 | 0.222027 | 0.606584 | 0.084761 | 2.710 | 0.193167 | 0.560798 | 0.068854 |
| 2.515 | 0.221262 | 0.605431 | 0.084320 | 2.715 | 0.192490 | 0.559664 | 0.068498 |
| 2.520 | 0.220500 | 0.604279 | 0.083881 | 2.720 | 0.191815 | 0.558530 | 0.068145 |
| 2.525 | 0.219739 | 0.603127 | 0.083445 | 2.725 | 0.191142 | 0.557397 | 0.067793 |
| 2.530 | 0.218981 | 0.601975 | 0.083011 | 2.730 | 0.190471 | 0.556265 | 0.067443 |
| 2.535 | 0.218225 | 0.600824 | 0.082579 | 2.735 | 0.189802 | 0.555134 | 0.067095 |
| 2.540 | 0.217472 | 0.599673 | 0.082149 | 2.740 | 0.189135 | 0.554003 | 0.066749 |
| 2.545 | 0.216721 | 0.598522 | 0.081723 | 2.745 | 0.188470 | 0.552873 | 0.066405 |
| 2.550 | 0.215972 | 0.597372 | 0.081299 | 2.750 | 0.187808 | 0.551743 | 0.066063 |
| 2.555 | 0.215225 | 0.596222 | 0.080876 | 2.755 | 0.187147 | 0.550614 | 0.065722 |
| 2.560 | 0.214481 | 0.595072 | 0.080456 | 2.760 | 0.186488 | 0.549486 | 0.065383 |
| 2.565 | 0.213738 | 0.593923 | 0.080039 | 2.765 | 0.185832 | 0.548359 | 0.065046 |
| 2.570 | 0.212998 | 0.592774 | 0.079623 | 2.770 | 0.185177 | 0.547232 | 0.064711 |
| 2.575 | 0.212260 | 0.591625 | 0.079210 | 2.775 | 0.184525 | 0.546106 | 0.064378 |
| 2.580 | 0.211525 | 0.590477 | 0.078799 | 2.780 | 0.183874 | 0.544980 | 0.064047 |
| 2.585 | 0.210792 | 0.589330 | 0.078390 | 2.785 | 0.183226 | 0.543856 | 0.063717 |
| 2.590 | 0.210061 | 0.588183 | 0.077983 | 2.790 | 0.182579 | 0.542702 | 0.063389 |
| 2.595 | 0.209332 | 0.587036 | 0.077579 | 2.795 | 0.181935 | 0.541609 | 0.063062 |

## Table 5a (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 2.800 | 0.181293 | 0.540486 | 0.062738 | 2.900 | 0.168858 | 0.518203 | 0.056595 |
| 2.805 | 0.180652 | 0.539365 | 0.062415 | 2.905 | 0.168257 | 0.517097 | 0.056305 |
| 2.810 | 0.180014 | 0.538244 | 0.062093 | 2.910 | 0.167658 | 0.515993 | 0.056016 |
| 2.815 | 0.179377 | 0.537123 | 0.061774 | 2.915 | 0.167060 | 0.514889 | 0.055728 |
| 2.820 | 0.178743 | 0.536004 | 0.061456 | 2.920 | 0.166464 | 0.513786 | 0.055442 |
| 2.825 | 0.178110 | 0.534885 | 0.061140 | 2.925 | 0.165871 | 0.512685 | 0.055158 |
| 2.830 | 0.177480 | 0.533767 | 0.060826 | 2.930 | 0.165279 | 0.511584 | 0.054876 |
| 2.835 | 0.176851 | 0.532650 | 0.060513 | 2.935 | 0.164689 | 0.510484 | 0.054594 |
| 2.840 | 0.176225 | 0.531534 | 0.060202 | 2.940 | 0.164101 | 0.509385 | 0.054314 |
| 2.845 | 0.175600 | 0.530419 | 0.059893 | 2.945 | 0.163514 | 0.508286 | 0.054036 |
| 2.850 | 0.174978 | 0.529304 | 0.059585 | 2.950 | 0.162930 | 0.507189 | 0.053759 |
| 2.855 | 0.174357 | 0.528190 | 0.059279 | 2.955 | 0.162347 | 0.506093 | 0.053484 |
| 2.860 | 0.173738 | 0.527077 | 0.058974 | 2.960 | 0.161767 | 0.504997 | 0.053210 |
| 2.865 | 0.173122 | 0.525965 | 0.058671 | 2.965 | 0.161188 | 0.503903 | 0.052937 |
| 2.870 | 0.172507 | 0.524853 | 0.058370 | 2.970 | 0.160611 | 0.502810 | 0.052666 |
| 2.875 | 0.171894 | 0.523743 | 0.058070 | 2.975 | 0.160036 | 0.501717 | 0.052397 |
| 2.880 | 0.171283 | 0.522633 | 0.057772 | 2.980 | 0.159462 | 0.500625 | 0.052128 |
| 2.885 | 0.170674 | 0.521524 | 0.057475 | 2.985 | 0.158891 | 0.499535 | 0.051861 |
| 2.890 | 0.170067 | 0.520416 | 0.057180 | 2.990 | 0.158321 | 0.498445 | 0.051596 |
| 2.895 | 0.169462 | 0.519309 | 0.056887 | 2.995 | 0.157753 | 0.497357 | 0.051332 |
| | | | | 3.000 | 0.157187 | 0.496269 | 0.051069 |

## Table 5b. A Six-Place Table of the Einstein Function $x$ at Intervals of 0.01

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 3.00 | 0.157187 | 0.496269 | 0.051069 | 3.40 | 0.117387 | 0.412894 | 0.033943 |
| 3.01 | 0.156060 | 0.494097 | 0.050548 | 3.41 | 0.116520 | 0.410912 | 0.033599 |
| 3.02 | 0.154941 | 0.491929 | 0.050032 | 3.42 | 0.115660 | 0.408935 | 0.033259 |
| 3.03 | 0.153829 | 0.489764 | 0 049522 | 3.43 | 0.114805 | 0.406963 | 0.032923 |
| 3.04 | 0 152724 | 0.487604 | 0 049017 | 3.44 | 0.113956 | 0.404996 | 0.032590 |
| 3.05 | 0.151626 | 0.485448 | 0.048517 | 3.45 | 0.113113 | 0.403036 | 0.032260 |
| 3.06 | 0.150535 | 0.483296 | 0.048022 | 3.46 | 0.112276 | 0.401080 | 0.031934 |
| 3.07 | 0.149451 | 0.481149 | 0.047533 | 3.47 | 0.111444 | 0.399130 | 0.031611 |
| 3.08 | 0.148374 | 0.479006 | 0.047049 | 3 48 | 0.110618 | 0.397186 | 0.031292 |
| 3.09 | 0.147304 | 0.476867 | 0.046570 | 3.49 | 0.109797 | 0.395247 | 0.030976 |
| 3.10 | 0.146241 | 0.474732 | 0.046095 | 3.50 | 0.108982 | 0.393313 | 0.030663 |
| 3.11 | 0.145184 | 0.472602 | 0.045626 | 3.51 | 0.108172 | 0.391386 | 0.030353 |
| 3.12 | 0.144135 | 0.470476 | 0.045162 | 3.52 | 0.107368 | 0.389463 | 0.030046 |
| 3.13 | 0.143092 | 0.468355 | 0.044702 | 3.53 | 0.106569 | 0.387547 | 0.029743 |
| 3.14 | 0.142057 | 0.466238 | 0.044247 | 3.54 | 0.105776 | 0.385636 | 0.029443 |
| 3.15 | 0.141028 | 0.464125 | 0.043797 | 3.55 | 0.104988 | 0.383731 | 0.029145 |
| 3.16 | 0.140005 | 0.462018 | 0.043352 | 3.56 | 0.104206 | 0.381831 | 0.028851 |
| 3.17 | 0.138989 | 0.459915 | 0.042911 | 3.57 | 0.103429 | 0.379937 | 0.028560 |
| 3.18 | 0.137980 | 0.457816 | 0.042475 | 3.58 | 0.102657 | 0.378049 | 0.028272 |
| 3.19 | 0 136978 | 0.455722 | 0 042043 | 3.59 | 0.101890 | 0.376167 | 0.027986 |
| 3.20 | 0.135982 | 0.453633 | 0.041616 | 3.60 | 0.101129 | 0.374290 | 0.027704 |
| 3.21 | 0.134993 | 0.451549 | 0.041194 | 3.61 | 0.100372 | 0.372419 | 0.027424 |
| 3.22 | 0.134010 | 0.449470 | 0.040775 | 3.62 | 0.099621 | 0.370554 | 0.027148 |
| 3.23 | 0.133033 | 0.447395 | 0.040361 | 3.63 | 0.098876 | 0.368695 | 0.026874 |
| 3.24 | 0.132063 | 0.445325 | 0.039951 | 3.64 | 0.098135 | 0.366841 | 0.026603 |
| 3.25 | 0.131099 | 0.443260 | 0.039546 | 3.65 | 0.097399 | 0.364993 | 0.026335 |
| 3.26 | 0.130142 | 0.441200 | 0.039145 | 3.66 | 0.096669 | 0.363152 | 0.026069 |
| 3.27 | 0.129191 | 0.439145 | 0.038748 | 3.67 | 0.095943 | 0.361316 | 0.025807 |
| 3.28 | 0.128246 | 0.437095 | 0.038355 | 3.68 | 0.095222 | 0.359485 | 0.025546 |
| 3.29 | 0.127308 | Q.435050 | 0.037966 | 3.69 | 0.094507 | 0.357661 | 0.025289 |
| 3.30 | 0.126376 | 0.433010 | 0.037581 | 3.70 | 0.093796 | 0.355843 | 0.025034 |
| 3.31 | 0.125449 | 0.430975 | 0.037200 | 3.71 | 0.093090 | 0.354031 | 0.024782 |
| 3.32 | 0.124529 | 0.428945 | 0.036823 | 3.72 | 0.092389 | 0.352224 | 0.024532 |
| 3.33 | 0.123616 | 0.426921 | 0.036449 | 3.73 | 0.091693 | 0.350424 | 0.024285 |
| 3.34 | 0.122708 | 0.424901 | 0.036080 | 3.74 | 0.091002 | 0.348629 | 0.024041 |
| 3.35 | 0.121806 | 0.422887 | 0.035715 | 3.75 | 0.090316 | 0.346840 | 0.023799 |
| 3.36 | 0.120910 | 0.420878 | 0.035353 | 3.76 | 0.089634 | 0.345058 | 0.023559 |
| 3.37 | 0.120021 | 0.418874 | 0.034995 | 3.77 | 0.088957 | 0.343281 | 0.023322 |
| 3.38 | 0.119137 | 0.416876 | 0.034641 | 3.78 | 0.088285 | 0.341510 | 0.023087 |
| 3.39 | 0.118259 | 0.414882 | 0.034290 | 3.79 | 0.087617 | 0.339746 | 0.022855 |

## Table 5b (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 3.80 | 0.086954 | 0.337987 | 0.022625 | 4.20 | 0.063940 | 0.272637 | 0.015109 |
| 3.81 | 0.086296 | 0.336234 | 0.022397 | 4.21 | 0.063445 | 0.271129 | 0.014958 |
| 3.82 | 0.085642 | 0.334488 | 0.022172 | 4.22 | 0.062954 | 0.269627 | 0.014808 |
| 3.83 | 0.084993 | 0.332747 | 0.021949 | 4.23 | 0.062466 | 0.268132 | 0.014659 |
| 3.84 | 0.084348 | 0.331012 | 0.021728 | 4.24 | 0.061981 | 0.266642 | 0.014512 |
| 3.85 | 0.083708 | 0.329284 | 0.021509 | 4.25 | 0.061500 | 0.265158 | 0.014367 |
| 3.86 | 0.083073 | 0.327561 | 0.021293 | 4.26 | 0.061023 | 0.263681 | 0.014223 |
| 3.87 | 0.082441 | 0.325845 | 0.021079 | 4.27 | 0.060549 | 0.262210 | 0.014080 |
| 3.88 | 0.081815 | 0.324135 | 0.020867 | 4.28 | 0.060078 | 0.260744 | 0.013939 |
| 3.89 | 0.081192 | 0.322431 | 0.020657 | 4.29 | 0.059611 | 0.259285 | 0.013800 |
| 3.90 | 0.080574 | 0.320733 | 0.020450 | 4.30 | 0.059147 | 0.257832 | 0.013661 |
| 3.91 | 0.079961 | 0.319041 | 0.020244 | 4.31 | 0.058687 | 0.256385 | 0.013525 |
| 3.92 | 0.079352 | 0.317355 | 0.020041 | 4.32 | 0.058230 | 0.254948 | 0.013389 |
| 3.93 | 0.078747 | 0.315675 | 0.019839 | 4.33 | 0.057776 | 0.253509 | 0.013255 |
| 3.94 | 0.078146 | 0.314001 | 0.019640 | 4.34 | 0.057326 | 0.252081 | 0.013122 |
| 3.95 | 0.077549 | 0.312333 | 0.019442 | 4.35 | 0.056879 | 0.250658 | 0.012991 |
| 3.96 | 0.076957 | 0.310672 | 0.019247 | 4.36 | 0.056435 | 0.249241 | 0.012861 |
| 3.97 | 0.076369 | 0.309017 | 0.019054 | 4.37 | 0.055994 | 0.247831 | 0.012732 |
| 3.98 | 0.075785 | 0.307367 | 0.018862 | 4.38 | 0.055557 | 0.246426 | 0.012604 |
| 3.99 | 0.075205 | 0.305724 | 0.018673 | 4.39 | 0.055123 | 0.245027 | 0.012478 |
| 4.00 | 0.074629 | 0.304087 | 0.018485 | 4.40 | 0.054692 | 0.243635 | 0.012353 |
| 4.01 | 0.074058 | 0.302456 | 0.018300 | 4.41 | 0.054264 | 0.242248 | 0.012230 |
| 4.02 | 0.073490 | 0.300832 | 0.018116 | 4.42 | 0.053839 | 0.240868 | 0.012107 |
| 4.03 | 0.072927 | 0.299213 | 0.017934 | 4.43 | 0.053418 | 0.239494 | 0.011986 |
| 4.04 | 0.072367 | 0.297601 | 0.017754 | 4.44 | 0.052999 | 0.238125 | 0.011866 |
| 4.05 | 0.071812 | 0.295995 | 0.017576 | 4.45 | 0.052584 | 0.236763 | 0.011747 |
| 4.06 | 0.071260 | 0.294394 | 0.017400 | 4.46 | 0.052171 | 0.235406 | 0.011630 |
| 4.07 | 0.070713 | 0.292800 | 0.017225 | 4.47 | 0.051762 | 0.234056 | 0.011513 |
| 4.08 | 0.070169 | 0.291213 | 0.017052 | 4.48 | 0.051356 | 0.232711 | 0.011398 |
| 4.09 | 0.069629 | 0.289631 | 0.016881 | 4.49 | 0.050952 | 0.231372 | 0.011284 |
| 4.10 | 0.069093 | 0.288055 | 0.016712 | 4.50 | 0.050552 | 0.230040 | 0.011171 |
| 4.11 | 0.068561 | 0.286486 | 0.016544 | 4.51 | 0.050155 | 0.228713 | 0.011059 |
| 4.12 | 0.068033 | 0.284923 | 0.016378 | 4.52 | 0.049760 | 0.227392 | 0.010949 |
| 4.13 | 0.067508 | 0.283365 | 0.016214 | 4.53 | 0.049369 | 0.226077 | 0.010839 |
| 4.14 | 0.066987 | 0.281814 | 0.016051 | 4.54 | 0.048980 | 0.224768 | 0.010731 |
| 4.15 | 0.066470 | 0.280270 | 0.015890 | 4.55 | 0.048594 | 0.223465 | 0.010623 |
| 4.16 | 0.065957 | 0.278731 | 0.015731 | 4.56 | 0.048211 | 0.222168 | 0.010517 |
| 4.17 | 0.065447 | 0.277198 | 0.015573 | 4.57 | 0.047831 | 0.220877 | 0.010412 |
| 4.18 | 0.064941 | 0.275672 | 0.015417 | 4.58 | 0.047454 | 0.219591 | 0.010308 |
| 4.19 | 0.064439 | 0.274152 | 0.015262 | 4.59 | 0.047080 | 0.218312 | 0.010205 |

## Table 5b (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 4.60 | 0.046708 | 0.217038 | 0.010103 | 5.00 | 0.033918 | 0.170742 | 0.006761 |
| 4.61 | 0.046339 | 0.215770 | 0.010002 | 5.01 | 0.033646 | 0.169697 | 0.006693 |
| 4.62 | 0.045973 | 0.214508 | 0.009902 | 5.02 | 0.033375 | 0.168657 | 0.006626 |
| 4.63 | 0.045609 | 0.213252 | 0.009803 | 5.03 | 0.033107 | 0.167623 | 0.006560 |
| 4.64 | 0.045249 | 0.212001 | 0.009705 | 5.04 | 0.032840 | 0.166594 | 0.006495 |
| 4.65 | 0.044891 | 0.210757 | 0.009608 | 5.05 | 0.032576 | 0.165570 | 0.006430 |
| 4.66 | 0.044535 | 0.209518 | 0.009512 | 5.06 | 0.032314 | 0.164551 | 0.006366 |
| 4.67 | 0.044183 | 0.208285 | 0.009416 | 5.07 | 0.032053 | 0.163537 | 0.006302 |
| 4.68 | 0.043833 | 0.207057 | 0.009322 | 5.08 | 0.031795 | 0.162529 | 0.006239 |
| 4.69 | 0.043485 | 0.205836 | 0.009229 | 5.09 | 0.031539 | 0.161526 | 0.006177 |
| 4.70 | 0.043140 | 0.204620 | 0.009138 | 5.10 | 0.031284 | 0.160528 | 0.006115 |
| 4.71 | 0.042798 | 0.203410 | 0.009046 | 5.11 | 0.031032 | 0.159535 | 0.006054 |
| 4.72 | 0.042458 | 0.202205 | 0.008955 | 5.12 | 0.030781 | 0.158547 | 0.005994 |
| 4.73 | 0.042121 | 0.201006 | 0.008866 | 5.13 | 0.030533 | 0.157564 | 0.005934 |
| 4.74 | 0.041786 | 0.199813 | 0.008777 | 5.14 | 0.030286 | 0.156587 | 0.005875 |
| 4.75 | 0.041454 | 0.198626 | 0.008689 | 5.15 | 0.030041 | 0.155614 | 0.005816 |
| 4.76 | 0.041125 | 0.197444 | 0.008603 | 5.16 | 0.029798 | 0.154647 | 0.005758 |
| 4.77 | 0.040797 | 0.196268 | 0.008517 | 5.17 | 0.029557 | 0.153685 | 0.005701 |
| 4.78 | 0.040473 | 0.195097 | 0.008431 | 5.18 | 0.029318 | 0.152727 | 0.005644 |
| 4.79 | 0.040150 | 0.193933 | 0.008347 | 5.19 | 0.029081 | 0.151775 | 0.005588 |
| 4.80 | 0.039831 | 0.192773 | 0.008264 | 5.20 | 0.028845 | 0.150827 | 0.005532 |
| 4.81 | 0.039513 | 0.191620 | 0.008181 | 5.21 | 0.028612 | 0.149885 | 0.005477 |
| 4.82 | 0.039198 | 0.190471 | 0.008099 | 5.22 | 0.028380 | 0.148948 | 0.005422 |
| 4.83 | 0.038885 | 0.189329 | 0.008019 | 5.23 | 0.028150 | 0.148015 | 0.005368 |
| 4.84 | 0.038575 | 0.188192 | 0.007938 | 5.24 | 0.027921 | 0.147087 | 0.005314 |
| 4.85 | 0.038267 | 0.187060 | 0.007859 | 5.25 | 0.027695 | 0.146165 | 0.005261 |
| 4.86 | 0.037962 | 0.185934 | 0.007781 | 5.26 | 0.027470 | 0.145247 | 0.005209 |
| 4.87 | 0.037658 | 0.184814 | 0.007703 | 5.27 | 0.027247 | 0.144334 | 0.005157 |
| 4.88 | 0.037357 | 0.183699 | 0.007626 | 5.28 | 0.027026 | 0.143426 | 0.005105 |
| 4.89 | 0.037059 | 0.182589 | 0.007550 | 5.29 | 0.026806 | 0.142523 | 0.005054 |
| 4.90 | 0.036762 | 0.181485 | 0.007475 | 5.30 | 0.026588 | 0.141624 | 0.005004 |
| 4.91 | 0.036468 | 0.180387 | 0.007400 | 5.31 | 0.026372 | 0.140731 | 0.004954 |
| 4.92 | 0.036176 | 0.179294 | 0.007326 | 5.32 | 0.026157 | 0.139842 | 0.004905 |
| 4.93 | 0.035886 | 0.178206 | 0.007253 | 5.33 | 0.025945 | 0.138958 | 0.004856 |
| 4.94 | 0.035598 | 0.177123 | 0.007181 | 5.34 | 0.025733 | 0.138078 | 0.004807 |
| 4.95 | 0.035313 | 0.176046 | 0.007109 | 5.35 | 0.025524 | 0.137204 | 0.004759 |
| 4.96 | 0.035030 | 0.174975 | 0.007038 | 5.36 | 0.025316 | 0.136334 | 0.004712 |
| 4.97 | 0.034749 | 0.173909 | 0.006968 | 5.37 | 0.025110 | 0.135469 | 0.004665 |
| 4.98 | 0.034470 | 0.172848 | 0.006898 | 5.38 | 0.024905 | 0.134608 | 0.004618 |
| 4.99 | 0.034193 | 0.171792 | 0.006829 | 5.39 | 0.024702 | 0.133752 | 0.004572 |

## Table 5b (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 5.40 | 0.024500 | 0.132901 | 0.004527 | 5.80 | 0.017613 | 0.102466 | 0.003032 |
| 5.41 | 0.024300 | 0.132055 | 0.004482 | 5.81 | 0.017467 | 0.101791 | 0.003002 |
| 5.42 | 0.024102 | 0.131213 | 0.004437 | 5.82 | 0.017323 | 0.101119 | 0.002972 |
| 5.43 | 0.023905 | 0.130376 | 0.004393 | 5.83 | 0.017179 | 0.100451 | 0.002942 |
| 5.44 | 0.023710 | 0.129543 | 0.004349 | 5.84 | 0.017037 | 0.099788 | 0.002913 |
| 5.45 | 0.023516 | 0.128715 | 0.004306 | 5.85 | 0.016896 | 0.099127 | 0.002884 |
| 5.46 | 0.023324 | 0.127891 | 0.004263 | 5.86 | 0.016756 | 0.098471 | 0.002855 |
| 5.47 | 0.023133 | 0.127072 | 0.004220 | 5.87 | 0.016617 | 0.097819 | 0.002827 |
| 5.48 | 0.022944 | 0.126257 | 0.004178 | 5.88 | 0.016479 | 0.097170 | 0.002799 |
| 5.49 | 0.022756 | 0.125447 | 0.004136 | 5.89 | 0.016343 | 0.096526 | 0.002771 |
| 5.50 | 0.022569 | 0.124642 | 0.004095 | 5.90 | 0.016207 | 0.095885 | 0.002743 |
| 5.51 | 0.022385 | 0.123840 | 0.004054 | 5.91 | 0.016073 | 0.095247 | 0.002716 |
| 5.52 | 0.022201 | 0.123044 | 0.004014 | 5.92 | 0.015939 | 0.094614 | 0.002689 |
| 5.53 | 0.022019 | 0.122251 | 0.003974 | 5.93 | 0.015807 | 0.093984 | 0.002662 |
| 5.54 | 0.021839 | 0.121463 | 0.003934 | 5.94 | 0.015676 | 0.093358 | 0.002635 |
| 5.55 | 0.021660 | 0.120680 | 0.003895 | 5.95 | 0.015545 | 0.092736 | 0.002609 |
| 5.56 | 0.021482 | 0.119901 | 0.003856 | 5.96 | 0.015416 | 0.092117 | 0.002583 |
| 5.57 | 0.021306 | 0.119126 | 0.003818 | 5.97 | 0.015288 | 0.091502 | 0.002558 |
| 5.58 | 0.021131 | 0.118355 | 0.003780 | 5.98 | 0.015161 | 0.090891 | 0.002532 |
| 5.59 | 0.020957 | 0.117589 | 0.003742 | 5.99 | 0.015035 | 0.090283 | 0.002507 |
| 5.60 | 0.020785 | 0.116827 | 0.003705 | 6.00 | 0.014909 | 0.089679 | 0.002482 |
| 5.61 | 0.020614 | 0.116070 | 0.003668 | 6.01 | 0.014785 | 0.089079 | 0.002457 |
| 5.62 | 0.020445 | 0.115317 | 0.003631 | 6.02 | 0.014662 | 0.088482 | 0.002433 |
| 5.63 | 0.020276 | 0.114567 | 0.003595 | 6.03 | 0.014540 | 0.087888 | 0.002408 |
| 5.64 | 0.020110 | 0.113823 | 0.003559 | 6.04 | 0.014419 | 0.087298 | 0.002384 |
| 5.65 | 0.019944 | 0.113082 | 0.003524 | 6.05 | 0.014299 | 0.086712 | 0.002361 |
| 5.66 | 0.019780 | 0.112346 | 0.003489 | 6.06 | 0.014180 | 0.086129 | 0.002337 |
| 5.67 | 0.019617 | 0.111613 | 0.003454 | 6.07 | 0.014061 | 0.085550 | 0.002314 |
| 5.68 | 0.019455 | 0.110885 | 0.003420 | 6.08 | 0.013944 | 0.084974 | 0.002291 |
| 5.69 | 0.019295 | 0.110161 | 0.003386 | 6.09 | 0.013828 | 0.084402 | 0.002268 |
| 5.70 | 0.019136 | 0.109442 | 0.003352 | 6.10 | 0.013712 | 0.083833 | 0.002245 |
| 5.71 | 0.018978 | 0.108726 | 0.003318 | 6.11 | 0.013598 | 0.083267 | 0.002223 |
| 5.72 | 0.018822 | 0.108014 | 0.003285 | 6.12 | 0.013484 | 0.082705 | 0.002201 |
| 5.73 | 0.018666 | 0.107307 | 0.003252 | 6.13 | 0.013372 | 0.082146 | 0.002179 |
| 5.74 | 0.018512 | 0.106603 | 0.003220 | 6.14 | 0.013260 | 0.081591 | 0.002157 |
| 5.75 | 0.018359 | 0.105904 | 0.003188 | 6.15 | 0.013149 | 0.081039 | 0.002136 |
| 5.76 | 0.018208 | 0.105208 | 0.003156 | 6.16 | 0.013039 | 0.080490 | 0.002114 |
| 5.77 | 0.018057 | 0.104517 | 0.003125 | 6.17 | 0.012930 | 0.079945 | 0.002093 |
| 5.78 | 0.017908 | 0.103829 | 0.003094 | 6.18 | 0.012823 | 0.079410 | 0.002073 |
| 5.79 | 0.017760 | 0.103146 | 0.003063 | 6.19 | 0.012714 | 0.078864 | 0.002052 |

## Table 5b (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 6.20 | 0.012608 | 0.078329 | 0.002031 | 6.60 | 0.008991 | 0.059419 | 0.001361 |
| 6.21 | 0.012502 | 0.077797 | 0.002011 | 6.61 | 0.008915 | 0.059005 | 0.001348 |
| 6.22 | 0.012398 | 0.077268 | 0.001991 | 6.62 | 0.008839 | 0.058593 | 0.001334 |
| 6.23 | 0.012294 | 0.076742 | 0.001971 | 6.63 | 0.008764 | 0.058184 | 0.001321 |
| 6 24 | 0.012191 | 0 076220 | 0.001952 | 6.64 | 0.008690 | 0.057777 | 0.001308 |
| 6.25 | 0.012089 | 0.075700 | 0.001932 | 6.65 | 0.008616 | 0.057373 | 0.001295 |
| 6.26 | 0.011987 | 0.075184 | 0.001913 | 6.66 | 0.008543 | 0.056972 | 0.001282 |
| 6.27 | 0.011887 | 0.074671 | 0.001894 | 6.67 | 0.008471 | 0.056573 | 0.001269 |
| 6.28 | 0.011787 | 0.074162 | 0.001875 | 6.68 | 0.008399 | 0.056177 | 0.001257 |
| 6.29 | 0 011688 | 0.073655 | 0.001856 | 6.69 | 0.008328 | 0.055783 | 0.001244 |
| 6.30 | 0.011590 | 0.073151 | 0.001838 | 6.70 | 0.008257 | 0.055392 | 0.001232 |
| 6.31 | 0.011493 | 0.072651 | 0.001820 | 6.71 | 0.008187 | 0.055003 | 0.001219 |
| 6.32 | 0.011396 | 0.072154 | 0.001802 | 6.72 | 0.008118 | 0.054617 | 0.001207 |
| 6.33 | 0.011300 | 0.071659 | 0.001784 | 6.73 | 0.008049 | 0.054223 | 0.001195 |
| 6.34 | 0.011205 | 0.071168 | 0.001766 | 6.74 | 0 007980 | 0.053852 | 0.001183 |
| 6.35 | 0.011111 | 0.070680 | 0.001748 | 6.75 | 0.007913 | 0.053473 | 0.001172 |
| 6.36 | 0.011018 | 0.070195 | 0.001731 | 6.76 | 0.007845 | 0.053097 | 0.001160 |
| 6.37 | 0.010925 | 0.069713 | 0.001714 | 6.77 | 0.007779 | 0.052723 | 0.001148 |
| 6.38 | 0.010833 | 0.069233 | 0.001697 | 6.78 | 0.007713 | 0.052352 | 0.001137 |
| 6.39 | 0.010742 | 0.068757 | 0.001680 | 6.79 | 0.007647 | 0.051983 | 0.001126 |
| 6.40 | 0.010652 | 0.068284 | 0.001663 | 6.80 | 0.007582 | 0.051616 | 0.001114 |
| 6.41 | 0.010562 | 0.067814 | 0.001646 | 6.81 | 0.007518 | 0.051252 | 0.001103 |
| 6.42 | 0.010473 | 0.067347 | 0.001630 | 6.82 | 0.007454 | 0.050890 | 0.001092 |
| 6.43 | 0.010385 | 0.066882 | 0.001614 | 6.83 | 0.007390 | 0.050530 | 0.001081 |
| 6.44 | 0.010297 | 0.066421 | 0.001598 | 6.84 | 0.007327 | 0.050173 | 0.001071 |
| 6.45 | 0.010211 | 0 065316 | 0.001582 | 6.85 | 0.007265 | 0.049818 | 0.001060 |
| 6.46 | 0 010124 | 0.065506 | 0.001566 | 6.86 | 0.007203 | 0.049465 | 0.001049 |
| 6.47 | 0 010039 | 0.065053 | 0.001550 | 6.87 | 0.007142 | 0.049115 | 0.001039 |
| 6.48 | 0 009954 | 0 064603 | 0.001535 | 6.88 | 0.007081 | 0.048767 | 0.001029 |
| 6.49 | 0 009870 | 0.064156 | 0 001520 | 6.89 | 0.007021 | 0.048421 | 0.001018 |
| 6.50 | 0 009787 | 0 063712 | 0.001505 | 6 90 | 0.006961 | 0.048078 | 0.001008 |
| 6.51 | 0 009704 | 0 063270 | 0 001490 | 6.91 | 0.006901 | 0.047736 | 0.000998 |
| 6.52 | 0 009623 | 0 062831 | 0 001475 | 6.92 | 0.006843 | 0 047397 | 0.000988 |
| 6.53 | 0 009541 | 0 062395 | 0.001460 | 6.93 | 0 006784 | 0 047060 | 0.000978 |
| 6.54 | 0 009461 | 0 061962 | 0 001446 | 6.94 | 0 006726 | 0 046726 | 0.000969 |
| 6.55 | 0 009381 | 0 061531 | 0 001431 | 6.95 | 0 006669 | 0.046393 | 0.000959 |
| 6.56 | 0 009301 | 0 061104 | 0.001417 | 6.96 | 0.006612 | 0.046063 | 0.000950 |
| 6.57 | 0 009223 | 0 060678 | 0 001403 | 6.97 | 0 006556 | 0.045735 | 0.000940 |
| 6.58 | 0 009145 | 0 060256 | 0.001389 | 6.98 | 0.006500 | 0.045409 | 0.000931 |
| 6.59 | 0 009067 | 0 059836 | 0 001375 | 6.99 | 0.006444 | 0.045085 | 0.000921 |

## Table 5b (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 7.00 | 0.006389 | 0.044764 | 0.000912 | 7.40 | 0.004526 | 0.033513 | 0.000611 |
| 7.01 | 0.006334 | 0.044444 | 0.000903 | 7.41 | 0.004487 | 0.033269 | 0.000605 |
| 7.02 | 0.006280 | 0.044127 | 0.000894 | 7.42 | 0.004448 | 0.033027 | 0.000599 |
| 7.03 | 0.006227 | 0.043812 | 0.000885 | 7.43 | 0.004410 | 0.032786 | 0.000593 |
| 7.04 | 0.006173 | 0.043498 | 0.000877 | 7.44 | 0.004372 | 0.032547 | 0.000587 |
| 7.05 | 0.006121 | 0.043187 | 0.000868 | 7.45 | 0.004334 | 0.032309 | 0.000582 |
| 7.06 | 0.006068 | 0.042878 | 0.000859 | 7.46 | 0.004297 | 0.032073 | 0.000576 |
| 7.07 | 0.006016 | 0.042571 | 0.000851 | 7.47 | 0.004260 | 0.031839 | 0.000570 |
| 7.08 | 0.005965 | 0.042266 | 0.000842 | 7.48 | 0.004223 | 0.031606 | 0.000564 |
| 7.09 | 0.005914 | 0.041963 | 0.000834 | 7.49 | 0.004187 | 0.031375 | 0.000559 |
| 7.10 | 0.005863 | 0.041662 | 0.000825 | 7.50 | 0.004150 | 0.031145 | 0.000553 |
| 7.11 | 0.005813 | 0.041363 | 0.000817 | 7.51 | 0.004115 | 0.030917 | 0.000548 |
| 7.12 | 0.005763 | 0.041066 | 0.000809 | 7.52 | 0.004079 | 0.030691 | 0.000542 |
| 7.13 | 0.005714 | 0.040771 | 0.000801 | 7.53 | 0.004044 | 0.030466 | 0.000537 |
| 7.14 | 0.005665 | 0.040478 | 0.000793 | 7.54 | 0.004009 | 0.030243 | 0.000531 |
| 7.15 | 0.005616 | 0.040187 | 0.000785 | 7.55 | 0.003974 | 0.030021 | 0.000526 |
| 7.16 | 0.005568 | 0.039898 | 0.000777 | 7.56 | 0.003940 | 0.029801 | 0.000521 |
| 7.17 | 0.005520 | 0.039611 | 0.000770 | 7.57 | 0.003906 | 0.029582 | 0.000516 |
| 7.18 | 0.005473 | 0.039326 | 0.000762 | 7.58 | 0.003872 | 0.029365 | 0.000511 |
| 7.19 | 0.005426 | 0.039042 | 0.000754 | 7.59 | 0.003839 | 0.029149 | 0.000506 |
| 7.20 | 0.005379 | 0.038761 | 0.000747 | 7.60 | 0.003805 | 0.028935 | 0.000501 |
| 7.21 | 0.005333 | 0.038481 | 0.000739 | 7.61 | 0.003772 | 0.028722 | 0.000496 |
| 7.22 | 0.005287 | 0.038204 | 0.000732 | 7.62 | 0.003740 | 0.028511 | 0.000491 |
| 7.23 | 0.005242 | 0.037928 | 0.000725 | 7.63 | 0.003707 | 0.028301 | 0.000486 |
| 7.24 | 0.005197 | 0.037654 | 0.000718 | 7.64 | 0.003675 | 0.028093 | 0.000481 |
| 7.25 | 0.005152 | 0.037382 | 0.000710 | 7.65 | 0.003643 | 0.027886 | 0.000476 |
| 7.26 | 0.005108 | 0.037111 | 0.000703 | 7.66 | 0.003612 | 0.027680 | 0.000471 |
| 7.27 | 0.005064 | 0.036843 | 0.000696 | 7.67 | 0.003581 | 0.027476 | 0.000467 |
| 7.28 | 0.005021 | 0.036576 | 0.000689 | 7.68 | 0.003550 | 0.027274 | 0.000462 |
| 7.29 | 0.004978 | 0.036311 | 0.000683 | 7.69 | 0.003519 | 0.027072 | 0.000457 |
| 7.30 | 0.004935 | 0.036053 | 0.000676 | 7.70 | 0.003488 | 0.026872 | 0.000453 |
| 7.31 | 0.004892 | 0.035787 | 0.000669 | 7.71 | 0.003458 | 0.026674 | 0.000448 |
| 7.32 | 0.004850 | 0.035527 | 0.000662 | 7.72 | 0.003428 | 0.026477 | 0.000444 |
| 7.33 | 0.004809 | 0.035269 | 0.000656 | 7.73 | 0.003398 | 0.026281 | 0.000440 |
| 7.34 | 0.004767 | 0.035013 | 0.000649 | 7.74 | 0.003369 | 0.026087 | 0.000435 |
| 7.35 | 0.004726 | 0.034759 | 0.000643 | 7.75 | 0.003340 | 0.025894 | 0.000431 |
| 7.36 | 0.004685 | 0.034507 | 0.000636 | 7.76 | 0.003311 | 0.025702 | 0.000427 |
| 7.37 | 0.004645 | 0.034256 | 0.000630 | 7.77 | 0.003282 | 0.025512 | 0.000422 |
| 7.38 | 0.004605 | 0.034006 | 0.000624 | 7.78 | 0.003253 | 0.025323 | 0.000418 |
| 7.39 | 0.004565 | 0.033759 | 0.000618 | 7.79 | 0.003225 | 0.025135 | 0.000414 |

**Table 5b (Continued)**

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x}$ |
|---|---|---|---|---|---|---|---|
| 7.80 | 0.003197 | 0.024949 | 0.000410 | 7.90 | 0.002930 | 0.023155 | 0.000371 |
| 7.81 | 0.003169 | 0.024764 | 0.000406 | 7.91 | 0.002904 | 0.022983 | 0.000367 |
| 7.82 | 0.003142 | 0.024580 | 0.000402 | 7.92 | 0.002879 | 0.022811 | 0.000363 |
| 7.83 | 0.003115 | 0.024397 | 0.000398 | 7.93 | 0.002854 | 0.022641 | 0.000360 |
| 7.84 | 0.003088 | 0.024216 | 0.000394 | 7.94 | 0.002829 | 0.022473 | 0.000356 |
| 7.85 | 0.003061 | 0.024036 | 0.000390 | 7.95 | 0.002805 | 0.022305 | 0.000353 |
| 7.86 | 0.003034 | 0.023858 | 0.000386 | 7.96 | 0.002780 | 0.022138 | 0.000349 |
| 7.87 | 0.003008 | 0.023680 | 0.000382 | 7.97 | 0.002756 | 0.021973 | 0.000346 |
| 7.88 | 0.002982 | 0.023504 | 0.000378 | 7.98 | 0.002732 | 0.021809 | 0.000342 |
| 7.89 | 0.002956 | 0.023329 | 0.000375 | 7.99 | 0.002708 | 0.021646 | 0.000339 |
| | | | | 8.00 | 0.002685 | 0.021484 | 0.000336 |

## Table 5c. A Six-Place Table of the Einstein Functions

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2 e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 8.00 | 0.002685 | 0.021484 | 0.000336 | 10.00 | 0.000454 | 0.004540 | 0.000045 |
| 8.05 | 0.002570 | 0.020692 | 0.000320 | 10.05 | 0.000434 | 0.004362 | 0.000043 |
| 8.10 | 0.002459 | 0.019927 | 0.000304 | 10.10 | 0.000415 | 0.004191 | 0.000041 |
| 8.15 | 0.002354 | 0.019190 | 0.000289 | 10.15 | 0.000397 | 0.004026 | 0.000039 |
| 8.20 | 0.002253 | 0.018478 | 0.000275 | 10.20 | 0.000379 | 0.003867 | 0.000037 |
| 8.25 | 0.002156 | 0.017791 | 0.000262 | 10.25 | 0.000362 | 0.003715 | 0.000035 |
| 8.30 | 0.002063 | 0.017129 | 0.000249 | 10.30 | 0.000346 | 0.003568 | 0.000034 |
| 8.35 | 0.001974 | 0.016490 | 0.000237 | 10.35 | 0.000331 | 0.003427 | 0.000032 |
| 8.40 | 0.001889 | 0.015874 | 0.000225 | 10.40 | 0.000317 | 0.003292 | 0.000030 |
| 8.45 | 0.001808 | 0.015280 | 0.000214 | 10.45 | 0.000303 | 0.003161 | 0.000029 |
| 8.50 | 0.001730 | 0.014707 | 0.000204 | 10.50 | 0.000289 | 0.003036 | 0.000028 |
| 8.55 | 0.001655 | 0.014154 | 0.000194 | 10.55 | 0.000276 | 0.002916 | 0.000026 |
| 8.60 | 0.001584 | 0.013621 | 0.000184 | 10.60 | 0.000264 | 0.002800 | 0.000025 |
| 8.65 | 0.001515 | 0.013108 | 0.000175 | 10.65 | 0.000252 | 0.002688 | 0.000024 |
| 8.70 | 0.001450 | 0.012613 | 0.000167 | 10.70 | 0.000241 | 0.002581 | 0.000023 |
| 8.75 | 0.001387 | 0.012136 | 0.000159 | 10.75 | 0.000231 | 0.002478 | 0.000021 |
| 8.80 | 0.001327 | 0.011676 | 0.000151 | 10.80 | 0.000221 | 0.002379 | 0.000020 |
| 8.85 | 0.001269 | 0.011233 | 0.000143 | 10.85 | 0.000211 | 0.002284 | 0.000019 |
| 8.90 | 0.001214 | 0 010806 | 0.000136 | 10.90 | 0.000201 | 0.002193 | 0.000018 |
| 8.95 | 0.001161 | 0 010395 | 0.000130 | 10.95 | 0.000192 | 0.002105 | 0.000018 |
| 9.00 | 0.001111 | 0.009999 | 0.000123 | 11.00 | 0.000184 | 0.002021 | 0.000017 |
| 9.05 | 0.001063 | 0.009617 | 0.000117 | 11.05 | 0.000176 | 0.001940 | 0.000016 |
| 9.10 | 0.001016 | 0.009249 | 0.000112 | 11.10 | 0.000168 | 0.001862 | 0.000015 |
| 9.15 | 0.000972 | 0.008895 | 0.000106 | 11.15 | 0.000160 | 0.001787 | 0.000014 |
| 9.20 | 0.000930 | 0.008554 | 0.000101 | 11.20 | 0.000153 | 0.001715 | 0.000014 |
| 9.25 | 0.000889 | 0.008225 | 0.000096 | 11.25 | 0.000146 | 0.001646 | 0.000013 |
| 9.30 | 0.000850 | 0.007909 | 0.000091 | 11.30 | 0.000140 | 0.001580 | 0.000012 |
| 9.35 | 0.000813 | 0.007604 | 0.000087 | 11.35 | 0.000134 | 0.001516 | 0.000012 |
| 9.40 | 0.000778 | 0.007311 | 0.000083 | 11.40 | 0.000128 | 0.001455 | 0.000011 |
| 9.45 | 0.000744 | 0.007028 | 0.000079 | 11.45 | 0.000122 | 0.001396 | 0.000011 |
| 9.50 | 0.000711 | 0.006756 | 0.000075 | 11.50 | 0.000116 | 0.001340 | 0.000010 |
| 9.55 | 0.000680 | 0.006495 | 0.000071 | 11.55 | 0.000111 | 0.001285 | 0.000010 |
| 9.60 | 0.000650 | 0.006243 | 0.000068 | 11.60 | 0.000106 | 0.001233 | 0.000009 |
| 9.65 | 0.000622 | 0.006000 | 0.000064 | 11.65 | 0.000102 | 0.001183 | 0.000009 |
| 9.70 | 0.000594 | 0.005767 | 0.000061 | 11.70 | 0.000097 | 0.001135 | 0.000008 |
| 9.75 | 0.000568 | 0.005542 | 0.000058 | 11.75 | 0.000093 | 0.001089 | 0.000008 |
| 9.80 | 0.000543 | 0.005326 | 0.000055 | 11.80 | 0.000089 | 0.001045 | 0.000008 |
| 9.85 | 0.000520 | 0.005118 | 0.000053 | 11.85 | 0.000085 | 0.001002 | 0.000007 |
| 9.90 | 0.000497 | 0.004918 | 0.000050 | 11.90 | 0.000081 | 0.000962 | 0.000007 |
| 9.95 | 0.000475 | 0.004726 | 0.000048 | 11.95 | 0.000077 | 0.000922 | 0.000006 |

## Table 5c (Continued)

| $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ | $x = \frac{h\nu_0}{kT}$ | $\frac{x}{e^x - 1}$ | $\frac{x^2e^x}{(e^x - 1)^2}$ | $-\ln(1-e^{-x})$ |
|---|---|---|---|---|---|---|---|
| 12.00 | 0.000074 | 0.000885 | 0.000006 | 13.50 | 0.000019 | 0.000250 | 0.000001 |
| 12.05 | 0.000070 | 0.000849 | 0.000006 | 13.55 | 0.000018 | 0.000239 | 0.000001 |
| 12.10 | 0.000067 | 0.000814 | 0.000006 | 13.60 | 0.000017 | 0.000229 | 0.000001 |
| 12.15 | 0.000064 | 0.000781 | 0.000005 | 13.65 | 0.000016 | 0.000220 | 0.000001 |
| 12.20 | 0.000061 | 0.000749 | 0.000005 | 13.70 | 0.000015 | 0.000211 | 0.000001 |
| 12.25 | 0.000059 | 0.000718 | 0.000005 | 13.75 | 0.000015 | 0.000202 | 0.000001 |
| 12.30 | 0.000056 | 0.000689 | 0.000005 | 13.80 | 0.000014 | 0.000193 | 0.000001 |
| 12.35 | 0.000053 | 0.000660 | 0.000004 | 13.85 | 0.000013 | 0.000185 | 0.000001 |
| 12.40 | 0.000051 | 0.000633 | 0.000004 | 13.90 | 0.000013 | 0.000178 | 0.000001 |
| 12.45 | 0.000049 | 0.000607 | 0.000004 | 13.95 | 0.000012 | 0.000170 | 0.000001 |
| 12.50 | 0.000047 | 0.000582 | 0.000004 | 14.00 | 0.000012 | 0.000163 | 0.000001 |
| 12.55 | 0.000044 | 0.000558 | 0.000004 | 14.05 | 0.000011 | 0.000156 | 0.000001 |
| 12.60 | 0.000042 | 0.000535 | 0.000003 | 14.10 | 0.000011 | 0.000150 | 0.000001 |
| 12.65 | 0.000041 | 0.000513 | 0.000003 | 14.15 | 0.000010 | 0.000143 | 0.000001 |
| 12.70 | 0.000039 | 0.000492 | 0.000003 | 14.20 | 0.000010 | 0.000137 | 0.000001 |
| 12.75 | 0.000037 | 0.000472 | 0.000003 | 14.25 | 0.000009 | 0.000132 | 0.000001 |
| 12.80 | 0.000035 | 0.000452 | 0.000003 | 14.30 | 0.000009 | 0.000126 | 0.000001 |
| 12.85 | 0.000034 | 0.000434 | 0.000003 | 14.35 | 0.000008 | 0.000121 | 0.000001 |
| 12.90 | 0.000032 | 0.000416 | 0.000002 | 14.40 | 0.000008 | 0.000116 | 0.000001 |
| 12.95 | 0.000031 | 0.000398 | 0.000002 | 14.45 | 0.000008 | 0.000111 | 0.000001 |
| 13.00 | 0.000029 | 0.000382 | 0.000002 | 14.50 | 0.000007 | 0.000106 | 0.000001 |
| 13.05 | 0.000028 | 0.000366 | 0.000002 | 14.55 | 0.000007 | 0.000102 | 0.000000 |
| 13.10 | 0.000027 | 0.000351 | 0.000002 | 14.60 | 0.000007 | 0.000097 | 0.000000 |
| 13.15 | 0.000026 | 0.000336 | 0.000002 | 14.65 | 0.000006 | 0.000093 | 0.000000 |
| 13.20 | 0.000024 | 0.000322 | 0.000002 | 14.70 | 0.000006 | 0.000089 | 0.000000 |
| 13.25 | 0.000023 | 0.000309 | 0.000002 | 14.75 | 0.000006 | 0.000085 | 0.000000 |
| 13.30 | 0.000022 | 0.000296 | 0.000002 | 14.80 | 0.000006 | 0.000082 | 0.000000 |
| 13.35 | 0.000021 | 0.000284 | 0.000002 | 14.85 | 0.000005 | 0.000078 | 0.000000 |
| 13.40 | 0.000020 | 0.000272 | 0.000002 | 14.90 | 0.000005 | 0.000075 | 0.000000 |
| 13.45 | 0.000019 | 0.000261 | 0.000001 | 14.95 | 0.000005 | 0.000072 | 0.000000 |
| | | | | 15.00 | 0.000005 | 0.000069 | 0.000000 |

## Table 6. *G* Function of Bigeleisen and Mayer[6]

| $u$ | $G$ | $\Delta G/\Delta u$ |
|---|---|---|
| 0.00 | .00000 | |
| .05 | .004165 | |
| .10 | .008415 | |
| .15 | .01265 | |
| .20 | .01671 | |
| .25 | .02075 | |
| .30 | .02496 | |
| .35 | .02910 | .0828 |
| .40 | .03326 | .0824 |
| .45 | .03738 | .0824 |
| .50 | .04150 | .0822 |
| .55 | .04561 | .0818 |
| .60 | .04970 | .0818 |
| .65 | .05379 | .0816 |
| .70 | .05787 | .0812 |
| .75 | .06193 | .0808 |
| .80 | .06597 | .0804 |
| .85 | .06999 | .0804 |
| .90 | .07401 | .0798 |
| .95 | .07800 | .0796 |
| 1.00 | .08198 | .0790 |
| 1.05 | .08593 | .0788 |
| 1.10 | .08987 | .0782 |
| 1.15 | .09378 | .0780 |
| 1.20 | .09768 | .0774 |
| 1.25 | .10155 | .0770 |
| 1.30 | .10540 | .0764 |
| 1.35 | .10922 | .0760 |
| 1.40 | .11302 | .0756 |
| 1.45 | .11680 | .0750 |
| 1.50 | .12055 | .0746 |
| 1.55 | .12428 | .0738 |
| 1.60 | .12797 | .0734 |
| 1.65 | .13164 | .0728 |
| 1.70 | .13528 | .0722 |
| 1.75 | .13889 | .0716 |
| 1.80 | .14247 | .0712 |
| 1.85 | .14603 | .0704 |
| 1.90 | .14955 | .0700 |
| 1.95 | .15305 | .0694 |
| 2.00 | .15652 | .0688 |
| 2.05 | .15996 | .0678 |
| 2.10 | .16335 | .0674 |
| 2.15 | .16672 | .0668 |
| 2.20 | .17006 | .0662 |
| 2.25 | .17337 | .0654 |
| 2.30 | .17665 | .0648 |
| 2.35 | .17989 | .0642 |
| 2.40 | .18310 | .0636 |
| 2.45 | .18628 | .0630 |
| 2.50 | .18943 | .0620 |
| 2.55 | .19253 | .0616 |
| 2.60 | .19561 | .0610 |
| 2.65 | .19866 | .0604 |
| 2.70 | .20168 | .0594 |
| 2.75 | .20465 | .0592 |
| 2.80 | .20761 | .0580 |
| 2.85 | .21051 | .0576 |
| 2.90 | .21339 | .0572 |
| 2.95 | .21625 | .0562 |
| 3.00 | .21906 | .0556 |
| 3.05 | .22184 | .0550 |
| 3.10 | .22459 | .0544 |
| 3.15 | .22731 | .0536 |
| 3.20 | .22999 | .0530 |
| 3.25 | .23264 | .0524 |
| 3.30 | .23526 | .0518 |
| 3.35 | .23785 | .0512 |
| 3.40 | .24041 | .0506 |
| 3.45 | .24294 | .0500 |
| 3.50 | .24544 | .0492 |
| 3.55 | .24790 | .0484 |
| 3.60 | .25032 | .0478 |
| 3.65 | .25271 | .0474 |
| 3.70 | .25508 | .0466 |
| 3.75 | .25741 | .0462 |
| 3.80 | .25972 | .0456 |
| 3.85 | .26200 | .0450 |
| 3.90 | .26425 | .0444 |
| 3.95 | .26647 | .0438 |
| 4.00 | .26866 | .0432 |
| 4.05 | .27082 | .0426 |
| 4.10 | .27295 | .0420 |
| 4.15 | .27505 | .0414 |
| 4.20 | .27712 | .0408 |
| 4.25 | .27919 | .0402 |
| 4.30 | .28119 | .0398 |
| 4.35 | .28318 | .0394 |
| 4.40 | .28515 | .0388 |
| 4.45 | .28709 | .0384 |
| 4.50 | .28901 | .0378 |
| 4.55 | .29090 | .0372 |
| 4.60 | .29276 | .0368 |
| 4.65 | .29460 | .0362 |
| 4.70 | .29641 | .0358 |
| 4.75 | .29820 | .0354 |
| 4.80 | .29997 | .0350 |
| 4.85 | .30172 | .0342 |
| 4.90 | .30343 | .0338 |
| 4.95 | .30512 | .0334 |
| 5.00 | .30679 | .0330 |
| 5.05 | .30844 | .0326 |
| 5.10 | .31007 | .0322 |
| 5.15 | .31168 | .0318 |
| 5.20 | .31327 | .0314 |
| 5.25 | .31484 | .0308 |
| 5.30 | .31638 | .0304 |
| 5.35 | .31790 | .0300 |
| 5.40 | .31940 | .0296 |
| 5.45 | .32088 | .0292 |
| 5.50 | .32234 | .0288 |
| 5.55 | .32378 | .0284 |
| 5.60 | .32520 | .0280 |
| 5.65 | .32660 | .0276 |
| 5.70 | .32798 | .0272 |
| 5.75 | .32934 | .0268 |
| 5.80 | .33068 | .0264 |
| 5.85 | .33200 | .0260 |
| 5.90 | .33330 | .0256 |
| 5.95 | .33458 | .0250 |
| 6.00 | .33583 | .0248 |
| 6.10 | .33831 | .0244 |
| 6.20 | .34075 | .0236 |
| 6.30 | .34311 | .0230 |
| 6.40 | .34541 | .0225 |
| 6.50 | .34766 | .0218 |
| 6.60 | .34984 | .0214 |
| 6.70 | .35198 | .0208 |
| 6.80 | .35406 | .0202 |
| 6.90 | .35608 | .0197 |
| 7.00 | .35805 | .0193 |
| 7.10 | .35998 | .0188 |
| 7.20 | .36186 | .0183 |
| 7.30 | .36369 | .0178 |
| 7.40 | .36547 | .0175 |
| 7.50 | .36722 | .0170 |
| 7.60 | .36892 | .0166 |
| 7.70 | .37058 | .0162 |
| 7.80 | .37220 | .0159 |
| 7.90 | .37379 | .0155 |
| 8.00 | .37534 | .0150 |
| 8.10 | .37684 | .0148 |
| 8.20 | .37832 | .0145 |
| 8.30 | .37977 | .0140 |
| 8.40 | .38117 | .0138 |
| 8.50 | .38255 | .0135 |
| 8.60 | .38390 | .0133 |
| 8.70 | .38523 | .0128 |
| 8.80 | .38651 | .0127 |
| 8.90 | .38778 | .0123 |
| 9.00 | .38901 | .0121 |
| 9.10 | .39022 | .0118 |
| 9.20 | .39140 | .0116 |
| 9.30 | .39256 | .0114 |
| 9.40 | .39370 | .0111 |
| 9.50 | .39481 | .0109 |
| 9.60 | .39590 | .0107 |
| 9.70 | .39697 | .0105 |
| 9.80 | .39802 | .0102 |

[6] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15,** 261 (1947).

**Table 6 (Continued)**

| $u$ | $G$ | $\Delta G/\Delta u$ | $u$ | $G$ | $\Delta G/\Delta u$ | $u$ | $G$ | $\Delta G/\Delta u$ |
|---|---|---|---|---|---|---|---|---|
| 9.90 | .39904 | .0101 | 15.00 | .43333 | .0044 | 20.10 | .45025 | .0025 |
| 10.00 | .40005 | .0098 | 15.10 | .43377 | .0044 | 20.20 | .45050 | .0024 |
| 10.10 | .40103 | .0097 | 15.20 | .43421 | .0043 | 20.30 | .45074 | .0024 |
| 10.20 | .40200 | .0094 | 15.30 | .43464 | .0042 | 20.40 | .45098 | .0024 |
| 10.30 | .40294 | .0094 | 15.40 | .43506 | .0042 | 20.50 | .45122 | .0024 |
| 10.40 | .40388 | .0091 | 15.50 | .43548 | .0042 | 20.60 | .45146 | .0023 |
| 10.50 | .40479 | .0089 | 15.60 | .43590 | .0041 | 20.70 | .45169 | .0023 |
| 10.60 | .40568 | .0088 | 15.70 | .43631 | .0040 | 20.80 | .45192 | .0023 |
| 10.70 | .40656 | .0087 | 15.80 | .43671 | .0040 | 20.90 | .45215 | .0023 |
| 10.80 | .40743 | .0085 | 15.90 | .43711 | .0039 | 21.00 | .45238 | .0023 |
| 10.90 | .40828 | .0083 | 16.00 | .43750 | .0039 | 21.10 | .45261 | .0022 |
| 11.00 | .40911 | .0082 | 16.10 | .43789 | .0038 | 21.20 | .45283 | .0022 |
| 11.10 | .40993 | .0079 | 16.20 | .43827 | .0038 | 21.30 | .45305 | .0022 |
| 11.20 | .41072 | .0079 | 16.30 | .43865 | .0037 | 21.40 | .45327 | .0022 |
| 11.30 | .41151 | .0078 | 16.40 | .43902 | .0037 | 21.50 | .45349 | .0021 |
| 11.40 | .41229 | .0076 | 16.50 | .43939 | .0037 | 21.60 | .45370 | .0022 |
| 11.50 | .41305 | .0075 | 16.60 | .43976 | .0036 | 21.70 | .45392 | .0021 |
| 11.60 | .41380 | .0074 | 16.70 | .44012 | .0036 | 21.80 | .45413 | .0021 |
| 11.70 | .41454 | .0072 | 16.80 | .44048 | .0035 | 21.90 | .45434 | .0021 |
| 11.80 | .41526 | .0072 | 16.90 | .44083 | .0035 | 22.00 | .45455 | .0020 |
| 11.90 | .41598 | .0070 | 17.00 | .44118 | .0034 | 22.10 | .45475 | .0020 |
| 12.00 | .41668 | .0068 | 17.10 | .44152 | .0034 | 22.20 | .45494 | .0021 |
| 12.10 | .41736 | .0067 | 17.20 | .44186 | .0034 | 22.30 | .45516 | .0020 |
| 12.20 | .41803 | .0067 | 17.30 | .44220 | .0033 | 22.40 | .45536 | .0020 |
| 12.30 | .41870 | .0065 | 17.40 | .44253 | .0033 | 22.50 | .45556 | .0019 |
| 12.40 | .41935 | .0065 | 17.50 | .44286 | .0032 | 22.60 | .45575 | .0020 |
| 12.50 | .42000 | .0063 | 17.60 | .44318 | .0032 | 22.70 | .45595 | .0019 |
| 12.60 | .42063 | .0063 | 17.70 | .44350 | .0032 | 22.80 | .45614 | .0019 |
| 12.70 | .42126 | .0061 | 17.80 | .44382 | .0031 | 22.90 | .45633 | .0019 |
| 12.80 | .42187 | .0061 | 17.90 | .44413 | .0031 | 23.00 | .45652 | .0019 |
| 12.90 | .42248 | .0060 | 18.00 | .44444 | .0031 | 23.10 | .45671 | .0019 |
| 13.00 | .42308 | .0058 | 18.10 | .44475 | .0030 | 23.20 | .45690 | .0018 |
| 13.10 | .42366 | .0058 | 18.20 | .44505 | .0031 | 23.30 | .45708 | .0018 |
| 13.20 | .42424 | .0057 | 18.30 | .44536 | .0029 | 23.40 | .45726 | .0019 |
| 13.30 | .42481 | .0056 | 18.40 | .44565 | .0030 | 23.50 | .45745 | .0018 |
| 13.40 | .42537 | .0056 | 18.50 | .44595 | .0029 | 23.60 | .45763 | .0018 |
| 13.50 | .42593 | .0054 | 18.60 | .44624 | .0028 | 23.70 | .45781 | .0017 |
| 13.60 | .42647 | .0054 | 18.70 | .44652 | .0029 | 23.80 | .45798 | .0018 |
| 13.70 | .42701 | .0053 | 18.80 | .44681 | .0028 | 23.90 | .45816 | .0017 |
| 13.80 | .42754 | .0052 | 18.90 | .44709 | .0028 | 24.00 | .45833 | .0018 |
| 13.90 | .42806 | .0051 | 19.00 | .44737 | .0027 | 24.10 | .45851 | .0017 |
| 14.00 | .42857 | .0051 | 19.10 | .44764 | .0028 | 24.20 | .45868 | .0017 |
| 14.10 | .42908 | .0050 | 19.20 | .44792 | .0027 | 24.30 | .45885 | .0017 |
| 14.20 | .42958 | .0049 | 19.30 | .44819 | .0026 | 24.40 | .45902 | .0016 |
| 14.30 | .43007 | .0049 | 19.40 | .44845 | .0027 | 24.50 | .45918 | .0017 |
| 14.40 | .43056 | .0047 | 19.50 | .44872 | .0026 | 24.60 | .45935 | .0016 |
| 14.50 | .43103 | .0048 | 19.60 | .44898 | .0026 | 24.70 | .45951 | .0017 |
| 14.60 | .43151 | .0046 | 19.70 | .44924 | .0025 | 24.80 | .45968 | .0016 |
| 14.70 | .43197 | .0046 | 19.80 | .44949 | .0026 | 24.90 | .45984 | .0016 |
| 14.80 | .43243 | .0046 | 19.90 | .44975 | .0025 | 25.00 | .46000 | |
| 14.90 | .43289 | .0044 | 20.00 | .45000 | .0025 | | | |

## Table 7. Some Useful Integrals

1. $\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}$, if $n$ is a positive integer, $a > 0$
2. $\int_0^\infty x^{2n} e^{-ax^2}\,dx = \frac{1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$
3. $\int_0^\infty e^{-ax^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$
4. $\int_0^\infty x e^{-ax^2}\,dx = \frac{1}{2a}$
5. $\int_0^\infty x^2 e^{-ax^2}\,dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$
6. $\int_0^\infty x^4 e^{-ax^2}\,dx = \frac{3}{8}\sqrt{\frac{\pi}{a^5}}$
7. $\int_0^\infty \frac{x}{e^x - 1}\,dx = \frac{\pi^2}{6}$
8. $\int_0^\infty \frac{x^2}{e^x - 1}\,dx = 2.40$
9. $\int_0^\infty \frac{x^3}{e^x - 1}\,dx = \frac{\pi^4}{15}$

# AUTHOR INDEX


Abraham, B. M., 207
Adams, N. I., Jr., 69
Allis, W. P., 81, 88, 89
Archibald, R. C., 188

Band, W., 211
Barrow, G. M., 190
Bartholomé, E., 129
Bigeleisen, J., 165, 166, 240
Bjerrum, N., 77, 188
Black, C. E., 189
Boltzmann, L., 4
Borie, B., 155–157
Brunauer, S., 202

Cassie, A. B. D., 196
Clusius, K., 129, 151
Collins, T. L., 221
Conway, B. E., 219

Daunt, J. G., 154
de Broglie, L., 102
Debye, P., 62–66, 70, 73–77, 143, 144, 148, 152, 153
Dennison, D. M., 130
DeSorbo, W., 150
Dole, M., 17, 189, 196, 204
d'Or, L., 134
Durgan, E. S., 178
Dworkin, A. S., 150

Edgar, G., 180
Einstein, A., 138, 140, 142, 211
Eldridge, J. A., 60
Emmett, P. H., 202
Estermann, I., 60
Eucken, A., 134
Ewell, R. B., 217

Flory, P. J., 24
Fowler, R. H., 32, 73, 75, 81, 172, 203, 206
Frey, F. E., 178

Giauque, W. F., 179, 180, 183, 188
Gibbs, J. W., 2, 4
Glasstone, S., 101
Goldmann, J., 151
Gordon, A. R., 188
Greiff, L. J., 77, 164, 167
Gronwall, T. H., 77
Gucker, F. T., Jr., 219
Guggenheim, E. A., 73, 75, 81, 172, 175, 177, 178, 203, 206
Guntelberg, E., 73
Gurney, R. W., 32, 38, 41, 50, 51, 55, 150
Gwinn, W. D., 173, 189

Halford, J. O., 173
Halsey, G., 204
Harned, H. S., 63, 77
Herlin, M. A., 81, 88, 89
Herzberg, G., 96, 117, 135, 137, 165, 179
Hettinger, W. P., Jr., 17
Hill, T. E., 196, 204
Hovorka, F., 76
Hückel, E., 62–66, 73–75
Hund, F., 130
Huppke, W. F., 178

Jäger, G., 67
Johnston, H. L., 219
Jura, G., 154

Kellerman, E. W., 153
Kemp, J. D., 188
Kilpatrick, J. E., 160, 161, 173, 189
Kistiakowsky, G. B., 178
Klotz, I. M., 1
Kuhn, W., 27

LaMer, V. K., 77
Langmuir, I., 180, 200
Larson, N. R., 17
Law, J. T., 150
Lewis, G. N., 76
London, F., 211

McCrea, J. M., 167
McMillan, W. G., 204

Maxwell, C., 4
Mayer, J. E., 5, 23, 32, 50, 88, 210, 212
Mayer, M. G., 5, 23, 32, 50, 88, 165, 166, 210, 212, 240
Mellor, J. W., 86
Mendelssohn, K., 154
Mizushima, S., 174
Montroll, E. W., 154
Morino, Y., 174

Nier, A. O., 221

Osborne, D. W., 207
Owen, B. B., 63, 77

Page, L., 69
Pauling, L., 187, 188, 219
Pease, R. N., 178
Perlick, A., 151
Person, W. B., 190
Pimentel, G. C., 190
Pitzer, K. S., 4, 50, 88, 154, 160, 161, 173, 177, 188–192

Randall, M., 76
Redlich, O., 165
Rice, J., 32
Roberts, L. D., 155–157
Rodebush, W. H., 76
Romeyn, H., Jr., 178
Rossini, F. D., 160, 161, 219, 222
Ruhemann, M., 154
Ruhoff, J. R., 178
Rushbrooke, G. S., 32

Saha, M. N., 180
Sandved, K., 77
Sartain, C. C., 155–157
Sasmor, D. J., 150
Schrödinger, E., 9, 48, 81–83, 90
Sherman, J., 217
Silvidi, A. A., 154
Simon, F., 154
Simpson, O. C., 60
Sips, R., 204
Slater, J. C., 100
Smith, H. A., 178
Stern, O., 60
Stout, J. W., 188

Takeda, M., 174
Tarasov, V. V., 150
Taylor, G. B., 30
Taylor, H. S., 204
Taylor, W. J., 160, 161
Teller, E., 165, 202, 204
Tolman, R. C., 1, 3, 4, 6, 9, 32
Tyler, W. W., 150

Urey, H. C., 164, 165, 167, 168, 170
Uspensky, J. V., 10, 21, 22

Van Artsdalen, E. R., 150
Vaughan, W. E., 178
Videnski (or Vvedenskii), A. A., 178
Vinal, G. W., 219
Vinikova (or Vinnikova), S. G., 178

Wagman, D. D., 160, 161
Waldmann, L., 165
Weinstock, B., 207
Weltner, W., Jr., 190–192
Wethington, J. A., Jr., 17
Wichers, E., 220
Witt, R. K., 188

# SUBJECT INDEX


Activity coefficient:
  Debye equation for, 75
  defined, 63
Adsorption, 194–205
  B.E.T., 202
  Freundlich, 204
  Langmuir, 196
  localized monolayer, 195, 196
  mobile monolayer, 194
  multilayer, 196–204
Angular momentum, 109, 170, 171
Anharmonicity correction factors, 167
  table of, 168
A priori probability, 18, 42
Arrangements, number of, 14
Association of ions, 77
Asymmetric top molecule, 96
Atomic weights, table of, 220
Averages:
  energy, 53, 54, 81, 82
  force, 84
  velocity, 60
Average values in statistical thermodynamics, 6
  defined, 52

B.E.T. adsorption, 202, 204
Binomial theorem, 19
Boltzmann distribution law, 43, 48, 50, 209
  quantum derivation of, 55
  various forms of, 57
Born lattice theory, 153
Boron nitride, heat capacity of, 151
Bose-Einstein statistics, 89, 90, 206–211
  distribution law, 209
  liquid helium and, 206, 207, 210, 211

Carbon dioxide:
  heat capacity, 135, 136
  isotope exchange equilibria, 169
  normal modes of vibration, 135
  potential energy, 117
Carbon monoxide:
  entropy of, 186
  heat capacity of, 133
Chemical energy, 37, 94, 116
Complexions:
  in Boltzmann statistics, 42
  in Bose-Einstein statistics, 208
  defined, 14
  in Fermi-Dirac statistics, 212
  general equation for, 16
Conjugate momenta, 3
Constants, universal, 219
Conversion factors for energy units, 222
Coulomb's law, 65, 78

Debye theory of the specific heat of solids, 143–153
  Debye $\theta$, 147
  $T$-cubed law, 148
  test of, 152, 153
Degeneracy:
  electronic, 134
  rotational, 36
  translational, 34
  vibrational, 36, 37
Degree of polymerization, 25, 26, 29
Deuterium:
  entropy, 185–187
  orientational spin wave functions, 126
  rotational partition function, 128
Dissociation energy:
  defined, 94, 117
  of hydrogen, 180
  methods of determining, 117–120
Distinguishability of particles, 41, 82
  in Bose-Einstein theory, 89, 207
Dulong and Petit, law of, 139

Einstein functions, table of, 223–239
Einstein theory:
  of degenerate gases, 211
  of specific heat of solids, 140–143
Electron gas, 212–214
  energy of, 213

Electron gas (*cont.*):
entropy of, at absolute zero, 213
pressure of, 213, 214
Electronic energy, 37
of NO, 134
of $O_2$, 134
Electronic partition function, 116
Energy of formation, 38, 94
of HCl, 95
Energy levels:
for the anharmonic oscillator, 117
electronic, 37
for rotation, 35
for rotational and vibrational states of hydrogen, 179
for translation, 33, 107
for vibration, 36
Energy units, table of, 222
Entropy:
of carbon monoxide, 186
defined, 86
of ethane, 188–190
of ethyl alcohol, 190
of hydrocarbons, 189, 190
of hydrogen, 183
of inorganic substances, table, 187
of isotope exchange, 184
of methyl alcohol, 190–193
of mixing, 184
of nitric oxide, 187
nuclear weights and, 184–186
orientational weights and, 186, 187
ortho and para hydrogen and, 184
probability and, 87
residual, table of, 187
rotational contribution to, 161, 162
rotational weights and, 185
in terms of partition function, 86
translational contribution to, 161
of water, 187–188
Equilibrium constants, 159–182
ethane, hydrogen, ethylene equilibrium, 175
and free energy, 159
hydrogen dissociation, 179, 180
isotopic exchange, 163–170
and symmetry numbers, 122, 163, 169
in terms of partition functions, 121, 159
Ethane:
entropy of, 188–190
equilibrium with hydrogen and ethylene, 176
internal rotation in, 170–173
normal modes of vibration, 177
physical constants for, 175
thermodynamic functions for, 177, 178
Ethyl alcohol:
entropy of, 190
rotational barriers in, 173
Ethylene:
equilibrium with hydrogen and ethane, 175
normal modes of vibration, 176
physical constants of, 175
thermodynamic functions for, 177, 178
Eulerian angles, 109, 110
Euler's criterion of integrability, 86

Factorial numbers:
defined, 13
properties of, 21
Fermi-Dirac statistics, 211–215
distribution law, 17, 212
electrons in metals and, 212–214
liquid helium and, 206, 207, 210, 214, 215
Fourth virial coefficient, 191
Free energy:
of adsorbed monolayer, 194, 195
of electron gas, 214
and equilibrium constant, 159
functions, 160–162
rotational contribution to, 114, 115, 161, 162
in terms of partition functions, 91, 159
translational contribution to, 108, 161
vibrational contribution to, 115
Frequency spectrum in solids, 153
Freundlich adsorption, 204

Gamma space, 4, 5
Generalized coordinates and momenta, 3
*G*-function of Bigeleisen and Mayer:
defined, 166
table of, 240, 241
Graphite, heat capacity of, 150, 151
Guntelberg charging process, 74

Hamiltonian function, 3
Heat capacity, 91
  at constant magnetization, 156
  of diatomic gases, 132–134
  electronic contribution, 134
  of electrons in metals, 154, 213
  of polyatomic gases, 135–138
  rotational of HD, 129
  rotational of hydrogen, 130, 131
  of solid hydrogen, 154, 155
  of solids, Debye theory, 143–150
  of solids, Einstein theory, 138–143
  in terms of partition functions, 91
  of two dimensional solids, 150, 151
Heat content, 91
  functions of, 160
  rotational contribution to, 161, 162
  in terms of partition functions, 91
  translational contribution to, 161
Helium:
  adsorption of, 211
  in Bose-Einstein statistics, 210, 211
  in Fermi-Dirac statistics, 214, 215
  properties of liquid $He^3$ and $He^4$, 210, 211
Hydrocarbons:
  entropy of, 189, 190
  frequencies of, 190
  moments of inertia of, 190
Hydrogen:
  dissociation equilibrium, 179, 180
  entropy, 183–186
  equilibrium with ethylene and ethane, 175
  heat capacity of, 131–133
  heat capacity of solid, 154, 155
  ortho and para, 124–131, 154
  physical constants for, 175
  rotational partition function, 128
  rotational states, 179
  spin wave functions, 126
  thermodynamic functions for, 177, 178
  vibrational states, 119, 179
Hydrogen bonding in methyl alcohol, 191, 192
Hydrogen chloride, potential energy diagram for, 95

Ice, entropy of, 187, 188
Indistinguishability of particles, 16, 82, 89, 90, 207
Integrals, table of, 242
Interaction:
  horizontal, 204
  vertical, 204
Interionic attraction theory of strong electrolytes, 62–77
Internal rotation, 170–175
Isotopic exchange equilibrium constants, 163–170
Isotopic fractionation factor, 169
Isotopic masses, table of, 221
Isotopic molecules:
  frequencies of vibration of, 165 (table, 168)
  moments of inertia of, 164

Kappa, Debye, 69, 72, 73

Lambda point, in liquid helium, 210
Lattice theory, Born, 153
Limiting law of Debye theory, 75
  extensions of, 77
Linear harmonic oscillator, 98
Liouville's theorem, 4–6

Magnetic field of nuclei, 125, 130
Maximum probability, 41, 48, 90
Maxwell velocity distribution equation, 57–59
Methane:
  deuteromethane, entropy of, 187
  entropy, 187
  heat capacity of, 137, 138
Methyl alcohol:
  corrections for nonideal behavior of, 190–193
  entropy of, 193
  hydrogen bonding of, 191, 192
  rotational barrier in, 173
Molecular weight distribution, 26–29
  number fraction, 27
  weight fraction, 28
Molecular weights:
  number average, 30
  weight average, 30
Moment of inertia, 96, 97, 189
  for hydrocarbons, table of, 190
  ratios of, for isotopic molecules, 164
Momentum space, condensation in, 211
Monolayer adsorption, 194–196

Multilayer adsorption, 196–205
B.E.T., 202
linear, 202
Mu-space, 4

Neodymium ethylsulfate, heat capacity of, 155, 156
Nitric oxide:
entropy of, 187
heat capacity of, 134
Nonideal gas behavior, corrections for, 190–193
Nuclear energy, 37
Nuclear spins:
entropy of, 185, 186, 187
statistical weight of, 125
table of, 221

Occupation numbers, 89
Ortho hydrogen, 124–131
entropy of, 185, 186
nuclear spin wave functions, 126
rotational partition function, 128
Oscillator:
anharmonic, 117
linear harmonic, 98–101, 172
partition function for, 113, 114
potential energy of, 98, 99, 172, 173
in solid state, 138, 139
wave equation for, 113
Oxygen:
entropy, 187
entropy of isotopic mixing, 184
heat capacity, 133, 134
isotopic exchange with water, 170

Para hydrogen, 124–131
entropy, 185, 186
nuclear spin wave function, 126
rotational partition function, 128
Particle in a box, 107
Partition function, 6, 7
defined, 50
electronic, 116
energy and, 81
entropy and, 86
explained, 51
factor for energy zero, 116–120
free energy and, 91
heat and, 85
heat capacity and, 91
internal rotational, 171
Partition function (*cont.*):
for perfect gas, 107
relation to thermodynamics, 91
rotational, 110, 111, 113
rotational, for ortho and para hydrogen, 128
summarized, 162
translational, 106, 108
vibrational, 113, 114
work and, 83
Perfect gas, 105
Permutations, 13
Phase space, 3–7
unit cell in, 100
Poisson equation, 67
Population of energy states, 38, 83, 207
in Bose-Einstein statistics, 208, 210
in Fermi-Dirac statistics, 211–214
vibrational states, 40
Potential energy:
for diatomic molecule, 94, 95
for linear harmonic oscillator, 98, 99
for restricted internal rotation, 172, 173
Probability, 10–21
compound, 12
of distribution of molecules, 41–43
entropy and, 87
of fluctuations, 44, 45
mathematical, 10, 88
maximum, 41, 48, 90
thermodynamic, 89, 208
total, 11
Product rule, 165

Quantum numbers:
rotational, 36
translational, 33, 34, 107
vibrational, 36

Raoult's law, 201
Reduced mass, 96, 97
relation to frequency, 165
Rotation:
internal, 170–175
kinetic energy of, 109
in the solid state, 149, 154
wave equation for, 112
Rotational contributions to thermodynamic functions, 114, 115, 161, 162

Rotational energy:
classical equation for, 35, 109
quantum equation for, 35, 112
Rotational isomers, 174
Rotational partition function:
diatomic molecules, 113
for homo- and heteronuclear molecules, 128
internal, 171
for ortho and para hydrogen, 128, 130
polyatomic molecules, 111

Schrödinger wave equation:
derivation of, 101
for the diatomic rotator, 112
for the linear harmonic oscillator, 113
for the particle in a box, 107
Second virial coefficient, 191
Specific heats (*see* Heat Capacity)
Spectroscopic entropy, 186
table of, 187
Spherical top molecule, 96
Spin:
of electron, 212
of nuclei, 125
table of nuclear spins, 221
Statistical mechanics, fundamental basis of, 2
Statistical thermodynamics:
defined, 7
limitations, 8
usefulness, 9
Statistical weight, 20, 42, 98, 106
entropy contribution, 184–187
of nuclear orientational states, 125, 126
of rotational states, 112
Stirling's approximation, 21
Symmetric top molecule, 96, 120–122
Symmetry number, 97
and equilibrium constants, 122
and isotopic exchange equilibria, 163, 169
and melting points, 97
quantum theory analog, 128
in the rotational partition function, 111
Symmetry properties of nuclei, 127, 128, 206
Symmetry of wave functions, 126

Teller-Redlich product rule, 165
Thermodynamic functions, 160–162
Thermodynamic probability:
defined, 89
in Bose-Einstein statistics, 208
Thermodynamics:
first, second, and third laws, 1
fundamental basis of, 1
limitations of, 2
relation to partition function, 90
Third law of thermodynamics, 1, 87
Translational contribution to free energy and entropy, 108
Translational energy:
average, 53–55
classical equations for, 34, 105
Schrödinger equation for, 33, 107
Translational partition function, 105–107

Uncertainty principle of Heisenberg, 4, 100
Undetermined multipliers, method of, 48, 49
in Bose-Einstein statistics, 209

Van der Waals force, 215
Velocities, average, 60
Vibrational contributions to thermodynamic functions, 114, 115
Vibrational energy:
quantum equation for, 36, 113, 117
vibrational-rotational energy states for hydrogen, 179
Vibrational partition function, 113, 114
Vibrational temperature, 37
Virial coefficients, 191, 192

Water:
entropy of, 187, 188
isotope exchange equilibria, 169, 170
Wave equation, 102
for the harmonic oscillator, 113
for the rigid rotator, 112
Schrödinger wave equation, 103
for translation, 107
Wave functions:
antisymmetric, 126

Wave functions (*cont.*)
for ortho and para deuterium, 126, 127
for ortho and para hydrogen, 125, 126
rotational, 127
symmetric, 126
Zero of energy, 94
methods of determining, 116–120
partition function factor for, 117
Zero point energy, 101
of anharmonic oscillator, 118
of electron gas, 213
of linear harmonic oscillator, 94

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